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Analyse mathématique. — *"Sur une propriété de séries trigonométriques."* By Prof. ARNAUD DENJOY.

(Communicated at the meeting of June 26, 1920).

Dans une Note que j'ai eu l'honneur de présenter à l'Académie dans sa dernière séance, j'ai démontré une propriété dont je vais rappeler l'énoncé, et qui appartient à une certaine classe de fonctions $F(\theta)$ *admettant une dérivée seconde généralisée* $f(\theta)$.

Posons

$$Q(\theta, u) = \frac{F(\theta + u) - F(\theta)}{u}$$

$$R(\theta, u) = \frac{F(\theta + u) + F(\theta - u) - 2F(\theta)}{u^2}.$$

On a $Q(\theta,u) = Q(\theta + u, -u)$ et $uR(\theta,u) = Q(\theta,u) - Q(\theta,-u)$. Par hypothèse $R(\theta,u)$ tend vers $f(\theta)$ quand u tend vers 0, θ restant invariable (condition A).

Nous désignons par $\psi(\theta)$ le maximum de $|R(\theta,u)|$ pour toutes les valeurs de u,θ gardant une valeur indépendante de u. η étant un nombre positif quelconque, $\psi(\theta,\eta)$ désignera le maximum de $|R(\theta,u)|$ pour $|u| < \eta$.

Les fonctions $F(\theta)$ auxquelles s'applique le théorème démontré dans ma précédente note, satisfont non seulement à la condition de posséder une dérivée seconde généralisée, mais encore à la suivante:

La différence $Q(\theta, \lambda u) - Q(\theta, u)$ *tend vers* 0 *avec* u, *uniformément dans tout champ*: θ *quelconque*, $|\lambda| + \left|\frac{1}{\lambda}\right| < r$, r *étant indépendant de* θ, *de* u *et de* λ (condition B).

Ces propriétés de $F(\theta)$ sont en particulier vérifiées si $f(\theta)$ est la somme d'une série trigonométrique partout convergente. Si l'on pose

$$f(\theta) = a_0 + A_1 + \ldots + A_n + \ldots, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

avec $A_n = a_n \cos n\theta + b_n \sin n\theta$ (a_0, a_n, b_n indépendants de θ), on a

$$F(\theta) = \frac{a_0}{2}\theta^2 + C\theta + C' - A_1 - \ldots - \frac{A_n}{n^2} - \ldots \quad . \quad . \quad (3)$$

(C, C' indépendants de θ).

Et si $\varphi(\theta)$ désigne, quand elle existe, la dérivée de $F(\theta)$,

$$\varphi(\theta) = a_0\theta + C + B_1 + \ldots + \frac{B_n}{n} + \ldots$$

avec

$$B_n = -b_n \cos n\theta + a_n \sin n\theta.$$

Les points θ de convergence de la série et d'existence de la dérivée sont les mêmes, avec égalité de la dérivée et de la série en ces points. Cela posé, nous avons démontré la proposition suivante:

Si $|h_n|$ *tend vers* 0 *en décroissant, si la série* $\left|\frac{h_n^2}{h_{n+1}}\right|$ *est absolument convergente, si* $\psi(\theta + h_n)$ *et* $\psi(\theta)$ *sont inférieurs à* A *indépendant de* n, *la fonction* $F(t)$ *possède pour* $t = \theta$ *une dérivée* $\varphi(\theta)$.

Si en outre le rapport $\left|\frac{h_n}{h_{n+1}}\right|$ *est inférieur à* α *indépendant de* n, *et si* $|h| < 2\alpha |h_1|$, *on a*

$$Q(\theta, h) = \varphi(\theta) + 20\delta\alpha Ah \qquad (\delta^2 < 1) \quad . \quad . \quad . \quad . \quad (9)$$

Enfin, si $|h| < \eta$, A *peut être remplacé par la borne supérieure des nombres* $\psi(\theta, \eta)$, $\psi(\theta + h_n, \eta)$ *pour* $|h_n| < \eta$.

L'hypothèse faite sur ψ n'implique pas l'existence de la dérivée seconde généraliste de $f(\theta)$. La démonstration exige la condition (B).

De la formule (9) nous déduirons certaines propriétés différentielles de $F(\theta)$ en nous aidant du théorème de Baire sur les fonctions limites de fonctions continues.

THÉORÈME. *Si* P *est un ensemble parfait (continu ou discontinu), l'ensemble* K *des points de* P *au voisinage desquels* $\psi(\theta)$, *supposé fini, est non borné sur* P, *cet ensemble est non dense sur* P.[1])

Voici le sens de cet énoncé. Nous disons qu'une fonction $g(\theta)$ n'est pas bornée sur P, au voisinage d'un point θ_0, s'il est possible de déterminer une suite θ_n de points *situés* sur P, tendant vers θ_0 quand n croît, et tels que $|g(\theta_n)|$ croisse indéfiniment. θ_0 appartient à P puisque P, étant parfait, contient ses points limites.

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[1]) Je rappelle qu'un ensemble est dit *fermé* s'il contient tous ses points limites, *dense en lui-même* s'il admet chacun de ses points pour point limite, *parfait* s'il est à la fois fermé et dense en lui-même.

On appelle *portion* de P tout ensemble parfait ϖ contenu dans P et renfermant tous les points de P compris entre les extrémités de ϖ.

On dit que l'ensemble E est *partout dense* sur l'ensemble parfait P, si toute portion de P contient des points de E. E est dit *dense* sur P, s'il est partout dense sur une portion au moins de P. E est dit *non dense* sur P, si dans toute portion de P il en existe une autre où E n'a pas de points. Si (E, P) désigne l'ensemble commun à E et à P, E est partout dense, est dense, ou est non dense sur P, selon que le dérivé de (E, P), — c'est-à-dire l'ensemble des points limites de (E, P) — ou bien coïncide avec P, ou bien contient une portion de P, ou bien n'en contient aucune.

On peut encore dire que, quelque soit N, dans toute portion de P contenant θ_0, existe un point θ_N où $|g(\theta_N)| > N$.

Si au voisinage d'un point θ_0 de P, $\psi(\theta)$ n'est pas bornée sur P, l'oscillation [1]) de $\psi(\theta)$ sur P au point θ_0 est infinie. Et réciproquement d'ailleurs.

Or, M. Baire a montré que si une fonction $\psi(\theta)$ est limite de fonctions continues, l'ensemble $K(\alpha)$ des points de P où l'oscillation de $\psi(\theta)$ sur P surpasse un nombre positif α donné est non dense sur P. *A fortiori*, l'ensemble K des points où l'oscillation de $\psi(\theta)$ est infinie, est-il non dense sur P.

Voici la démonstration de Baire dans ce cas particulier.

Soit K l'ensemble des points de P au voisinage desquels $\psi(\theta)$ n'est pas borné. K est évidemment fermé. Si K n'était pas non dense sur P, il existerait une portion P_1 de P qui serait contenue dans K. Nous définissons simultanément: une suite de points $\theta_1, \ldots, \theta_n, \ldots$, situés sur P_1, une suite de segments [2]) $s_0, s_1, \ldots$, le segment s_n étant intérieur à s_{n-1} et contenant lui-même θ_n à son intérieur, et une suite de nombres u_n, par cette règle récurrente: s_0 est un segment quelconque contenant des points de P_1. s_{n-1} étant supposé obtenu, nous définissons comme il suit θ_n, s_n, u_n. $\psi(\theta)$ étant non borné sur P_1, au voisinage de tout point de P_1, il existe sur P_1, intérieurement à s_{n-1}, un point θ_n où $\psi(\theta_n) > 2n$. D'après $\psi(\theta_n) = \underset{-\pi<u<\pi}{max.} |R(\theta_n, u)|$, il existe un nombre u_n non nul tel que $|R(\theta_n, u_n)| > n$. $R(\theta,u)$ étant continue par rapport à θ si $u \neq 0$, on peut entourer θ_n d'un segment s_n intérieur à s_{n-1}, inférieur en longueur à $^1/_2 s_{n-1}$ et en tout point θ duquel $|R(\theta,u_n)| > n$.

Il existe un point θ' (et un seul, puisque s_n tend vers 0 en longueur) intérieur à tous les segments s_n. θ' est la limite unique des points θ_n. Donc, θ' est sur P_1. Or, θ' appartenant à s_n quelque soit n, la suite $|R(\theta',u_n)|$ croit indéfiniment avec n, ce qui est contraire à l'existence de $\psi(\theta')$.

Donc K est non dense sur P. Dans toute portion de P il en existe une autre où K n'a pas de points et sur laquelle, par suite, $(\psi\theta)$ est bornée. Cette conclusion exige seulement que, pour chaque valeur de θ, les limites d'indétermination de $R(\theta,u)$ pour $u = 0$

[1]) L'*oscillation* de f *sur un ensemble* Q en un point limite θ_0 de Q, est l'écart des valeurs limites extrêmes de f (θ) quand θ tend vers θ_0 sans quitter Q. (θ peut coïncider une infinité de fois avec θ_0, si θ_0 appartientà Q) Si f supposée finie en tout point et en particulier au point θ_0, est non bornée sur Q au voisinage de θ_0, l'oscillation de f sur Q en θ_0 est évidemment infinie.

[2]) Je distingue le *segment* $\alpha\beta$ (ensemble $\alpha \leq x \leq \beta$) de l'*intervalle* $\alpha\beta$ (ensemble $\alpha < x < \beta$).

soient finies et non pas (condition A) toujours égales et finies.

Si F vérifie la condition (A), on montre par un raisonnement analogue au précédent, que *si en tout point de* P, $|f(\theta)|$ *est inférieur à un nombre fixe* C, *on peut trouver un nombre positif* η *tel que, si* $\psi(\theta,\eta)$ *est le maximum de* $|R(\theta,u)|$ *pour* $|u|<\eta$, *il existe une portion* P_1 *de* P *en tout point de laquelle* $\psi(\theta,\eta)<C$. L'hypothèse opposée, que toute portion de P contient, quelque soit η, des points θ où $\psi(\theta,\eta)\geq C$, entraîne $|f(\theta)|\geq C$ en certains points de P. Toute portion de P donne lieu au même énoncé que P lui-même.

Nous allons appliquer les propositions précédentes à diverses catégories d'ensembles parfaits P, *en supposant que* F *vérifie les conditions* (A) *et* (B).

Prenons d'abord pour P un segment continu $\alpha\beta$. L'ensemble K relatif à P est non dense sur P. Donc, dans tout segment S situé sur $\alpha\beta$, existe un segment s', ou $\alpha'\beta'$, où K ne possède aucun point. Alors, pour tous les points de s', $\psi(\theta)$ est inférieur à un même nombre A. θ et $\theta+h$ étant deux nombres quelconques intérieurs à s', posons $h_n=\frac{h}{2^n}$. D'après $\psi(\theta)$ et $\psi(\theta+h_n)<A$, F a une dérivée au point θ. De plus, d'après la formule (9) où $\alpha=2$ (et dont la démonstration se simplifierait extrémement avec les valeurs considérees de h_n),

$$Q(\theta,h)-\frac{F(\theta+h)-F(\theta)}{h}=\varphi(\theta)+40\delta Ah.$$

En échangeant les rôles de θ et de $\theta+h$, on trouve

$$Q(\varphi+h,-h)=\frac{F(\theta)-F(\theta+h)}{-h}=\varphi(\theta+h)+40\delta' Ah.\quad(\delta'^2,\delta''^2<1).$$

Par conséquent $\dfrac{\varphi(\theta+h)-\varphi(\theta)}{h}$ est borné sur l'intervalle $\alpha'\beta'$. Donc la fonction $\varphi(\theta)$ est continue sur s' et a ses nombres dérivés bornés. Elle possède, sauf éventuellement sur un ensemble de mesure nulle de valeurs de θ comprises entre α' et β', une dérivée qui, constituant pour F une dérivée seconde, ne saurait être autre que $f(\theta)$.

Nous obtenons donc ce premier résultat important:

1°. *L'ensemble des points de non existence ou de discontinuité de la dérivée de* $F(\theta)$, *est non dense sur le continu.*

2°. *L'ensemble des points autour desquels* $\varphi(\theta)$, *dérivée de* $F(\theta)$, *existe et est continue, et en lesquels* $\varphi(\theta)$ *a pour dérivée* $f(\theta)$, *cet ensemble est partout dense sur le continu.*

Je dis que l'ensemble des points où $F(\theta)$ ne possède pas de dérivée est de mesure nulle.

En effet, supposons que cet ensemble ait une mesure positive (qu'il soit *épais*)[1]. Il contient donc un ensemble parfait épais en lui-même P. Il existe une portion de P, soit P_1, où $\psi(\theta)$ est borné. Or P_1 étant épais, contient des points où son épaisseur est égale à 1. Soit θ_0 un de ces points. Il existe un nombre positif η, tel que, dans tout intervalle contenant θ_0 et de longueur inférieure à η, l'ensemble P_1 possède une épaisseur moyenne supérieure à $^1/_2$. Donc, dans l'intervalle $\theta_0 + \frac{\eta}{2^{n+1}}$ à $\theta_0 + \frac{\eta}{2^n}$, la mesure de P_1 est positive. Donc P_1 possède des points dans cet intervalle. Soit $\theta + h_n$ l'un d'eux. La suite h_n vérifie la condition $1 < \frac{h_n}{h_{n+1}} < 4$ et $\psi(\theta + h_n)$ est inférieur, quel que soit n, au maximum fini de $\psi(\theta)$ sur P.

Le théorème général s'applique. Donc, contrairement à notre hypothèse, $F(\theta)$ possède une dérivée en θ_0.

Donc, *l'ensemble E des points où $F'(\theta)$ n'existe pas, ensemble coïncidant avec celui où la série* (2) *diverge, cet ensemble est de mesure nulle*, résultat déjà connu et démontré en particulier par M. Fatou, mais que nous établissons sans recours à l'intégration.

Considérons l'ensemble E_1 où $\varphi(\theta)$ existe. Je dis que $\varphi(\theta)$ *possède une dérivée approximative*[2] *égale à $f(\theta)$ en tout point de E_1 sauf éventuellement sur un ensemble de mesure nulle*[3].

On montre d'abord par un type de raisonnement que j'ai indiqué

[1]) Je dis qu'un ensemble E est *épais* si sa mesure est positive; qu'il est *épais dans un intervalle ab*, si les points de E intérieurs à ab forment un ensemble de mesure positive; *épais en un point*, s'il est épais dans tout intervalle contenant ce point; *épais en lui-même*, s'il est épais en chacun de ses points. Si les points de E compris entre a et b $(a < b)$ forment un ensemble de mesure $m(b) - m(a)$, le rapport $\frac{m(b) - m(a)}{b - a}$ s'appelle l'*épaisseur moyenne* de E sur l'intervalle ab. L'*épaisseur* de E *en un point* x_0 est la limite, si elle existe, de l'épaisseur moyenne de E sur un intervalle contenant x_0 et tendant indifféremment vers 0 en longueur (voir ma note de la précédente séance pour les cas où l'épaisseur n'existe pas).

[2]) On dit que $\varphi(\theta)$ possède une *dérivée approximative* λ en un point θ_0 (où φ est définie) si le quotient $\frac{\varphi(\theta) - \varphi(\theta_0)}{\theta - \theta_0}$ tend vers λ, quand θ tend vers θ_0 en se déplaçant indifféremment sur un ensemble (où φ est supposé défini) dont l'épaisseur en θ_0 est égale à 1. (M. Kintchine emploie dans le même sens l'expression de dérivée asymptotique).

[3]) „Sur un ensemble contenu dans E_1 et de même mesure que lui" s'exprime par la locution „presque partout sur E_1" de M. Lebesque ou par celle-ci „sur une pleine épaisseur de E_1" que j'ai proposée.

ailleurs (Bull. de la Soc. Math. de Fr., 1915) que, si $\varphi(\theta)$ n'admet pas en θ_0 la dérivée approximative $f(\theta_0)$, il existe un nombre positif $d(\theta_0)$ ou d_0 tel que l'ensemble $e(d_0)$ des points θ vérifiant

$$\left| \frac{\varphi(\theta) - \varphi(\theta_0)}{\theta - \theta_0} - f(\theta_0) \right| > d(\theta_0)$$

possède en θ_0 une épaisseur supérieure positive, pour un côté au moins.

Si le théorème énoncé était inexact, l'ensemble H des points θ_0 précédents aurait une mesure positive.

Nous pouvons évidemment supposer que la fonction $d(\theta_0)$ de θ_0 est mesurable [il suffit pour cela que $d(\theta_0)$ soit par exemple la moitié de la borne supérieure stricte des nombres d tels que l'épaisseur supérieure en θ_0 de l'ensemble $e(d)$ soit positive]. Soit H_n l'ensemble des θ_0 tels que $nd(\theta_0) > 1$.

H est la réunion des H_n. Donc l'un au moins des H_n a une mesure positive. Il existe donc un nombre positif d, tel que l'ensemble H' des θ_0 vérifiant $d(\theta_0) > d$ a une mesure positive.

H' contient un ensemble parfait Q épais en lui-même.

$f(\theta)$ étant limite de fonctions continues est ponctuellement discontinue sur Q (Baire). Si petit que soit d', l'ensemble des points de Q où l'oscillation de $f(\theta)$ sur Q est au moins égale à d', cet ensemble est non dense sur Q. Prenons $d' = \frac{d}{121}$. Il existe une portion Q_1 de Q en tout point de laquelle l'oscillation de f sur Q (donc aussi sur Q_1) est inférieure à d'. Donc, si θ_1 est un point particulier de Q_1, il existe un intervalle i contenant θ_1 et tel qu'en chaque point θ de Q situé sur le segment i,

$$|f(\theta) - f(\theta_1)| < \frac{d}{121}$$

Soit Q_2 la portion de Q_1 déterminée par l'intervalle i. (Q_2 est l'ensemble parfait situé sur le *segment* i et coïncidant avec Q_1 dans *l'intervalle* i).

Chacun, sauf le dernier, des ensembles E_1, H, H', Q, Q_1, Q_2 contient le suivant. Donc, en tout point de Q_2, $\varphi(\theta)$ existe (puisque Q_2 est dans E_1), $f(\theta)$ est compris entre $f(\theta_1) - \frac{d}{121}$ et $f(\theta_1) + \frac{d}{121}$ (dernière condition de Q_2), et $\varphi(\theta)$ possède, en tout point θ_2 de Q_2, et sur tout ensemble $\omega(\theta_2)$ d'épaisseur 1 en θ_2, un nombre dérivé spécial à $\omega(\theta_2)$ et différant de $f(\theta)$ de plus de d en valeur absolue (puisque Q_2 est dans H').

Considérons $F_1(\theta) = F(\theta) - \frac{\theta^2}{2} f(\theta_1)$. Cette fonction continue possède en tout point de Q_2 la dérivée $\varphi_1(\theta) = \varphi(\theta) - \theta f(\theta_1)$. $F_1(\theta)$ possède

en tout point la dérivée seconde généralisée $f_1(\theta) = f(\theta) - f(\theta_1)$. $f_1(\theta)$ est compris, sur Q_2, entre $-\frac{d}{121}$ et $\frac{d}{121}$. D'autre part, les nombres dérivés de $\varphi_1(\theta)$ sont ceux de $\varphi(\theta)$ diminués de $f(\theta_1)$. Donc, $\varphi_1(\theta)$ dérivée de $F_1(\theta)$ existe en tout point de Q_2 et possède, quels que soient le point θ_2 de Q_2 et l'ensemble $\omega(\theta_2)$ ayant l'épaisseur 1 en θ_2, au moins un nombre dérivé spécial à $\omega(\theta_2)$ et différant de $f_1(\theta_2)$ d'au moins d en valeur absolue. Ce nombre dérivé vaut donc au moins $\frac{120}{121} d$ en valeur absolue.

D'après $|f_1(\theta)| < \frac{d}{121}$ quel que soit θ sur Q_2, il est possible de trouver un nombre $s' > 0$, tel que l'ensemble $\psi_1(\theta, s') < \frac{d}{121}$ contienne une portion K de Q_2. $\psi_1(\theta, s')$ est par définition le maximum de $R_1(\theta, u) = \frac{F_1(\theta + u) + F_1(\theta - u) - 2F_1(\theta)}{u^2}$ pour $0 < |u| < s'$.

L'ensemble parfait K jouit en résumé des propriétés suivantes :

1° K a une mesure positive (K étant portion de Q_2, épais en lui-même).

2° Il existe une fonction $F_1(\theta)$ et un nombre positif s' tel que la fonction $\psi_1(\theta, s')$ relative à F_1 est, en tout point de K, inférieure à $\frac{d}{121}$.

3° $F_1(\theta)$ possède en tout point de K une dérivée générale (ordinaire) $\varphi_1(\theta)$.

4° Quel que soit θ_0 sur K, et l'ensemble $\omega(\theta_0)$ d'épaisseur 1 en θ_0, $\varphi_1(\theta_0)$ possède en θ_0 un nombre dérivé spécial à $\omega(\theta_0)$ et dont la valeur absolue surpasse $\frac{120}{121} d$.

Nous allons montrer l'incompatibilité de ces conditions simultanées.

L'ensemble des points de K où K a l'épaisseur 1, a même mesure que K, donc une mesure positive. L'ensemble $j(s)$ des points θ_1 de K tels que, dans tout intervalle contenant θ_1 et de longueur inférieure à s (> 0), l'épaisseur de K soit supérieure à $\frac{5}{6}$, cet ensemble a une mesure positive dès que s est assez petit, et cette mesure tend vers celle de K quand s tend vers 0. Supposons $s < s'$ et $j(s)$ épais.

Soit θ_2 un point où $j(s)$ a lui-même l'épaisseur 1. Je dis que, si θ tend vers θ_2 sans quitter $j(s)$, $\frac{\varphi(\theta) \quad \varphi(\theta_2)}{\theta - \theta_2}$ a ses limites d'indétermi-

nation comprises entre $-\frac{120}{121}d$ et $\frac{120}{121}d$, ce qui est incompatible avec la 4e condition ci-dessus; car l'épaisseur de $j(s)$ en θ_2 est 1.

Supposons $|\theta - \theta_2| < s$, θ et θ_2 étant sur $j(s)$. Puisque K a une épaisseur supérieure à $\frac{5}{6}$ dans tout intervalle contenant θ ou θ_2 et de longueur inférieure à s, nous pouvons trouver sur K deux suites de nombres $\theta + h_n$, $\theta_2 + k_n$ de manière que

$$1^\circ.\ h_1 = -k_1 = \theta_2 - \theta, \quad 2^\circ.\ 2 \leq \left|\frac{h_n}{h_{n+1}}\right| \leq 3 \text{ et } 2 \leq \left|\frac{k_n}{k_{n+1}}\right| \leq 3.$$

D'après $\psi(\theta', s) < \frac{d}{121}$ quel que soit θ' sur K, on a donc $(\alpha = 3)$:

$$Q_1(\theta, \theta_2 - \theta) = \varphi_1(\theta) + 60\delta\frac{d}{121}(\theta_2 - \theta)$$

et de même

$$Q_1(\theta_2, \theta - \theta_2) = \varphi_1(\theta_2) + 60\,\delta'\frac{d}{121}(\theta - \theta_2).$$

D'après l'égalité des premiers membres de ces deux relations

$$\frac{\varphi_1(\theta) - \varphi_1(\theta_2)}{\theta - \theta_2} = 120\,\delta''\frac{d}{121} \qquad (\delta^2, \delta'^2, \delta''^2 < 1).$$

Cette relation est exacte quels que soient θ et θ_2 sur $j(s)$, si $|\theta - \theta_2| < s$. Donc les nombres dérivés de $\varphi_1(\theta)$ au point θ_2, spécialement à $j(s)$, sont inférieurs à $\frac{120}{121}d$ en valeur absolue, ce qui est opposé à l'hypothèse 4.

En résumé, *l'ensemble des points où $F(\theta)$ ne possède pas une dérivée ordinaire $\varphi(\theta)$ est de mesure nulle. Soit E cet ensemble, et E_1 son complémentaire. La fonction $\varphi(\theta)$, définie seulement sur E_1, possède une dérivée approximative égale à $f(\theta)$, sauf éventuellement en des points formant un ensemble de mesure nulle.*

Soit maintenant P un ensemble parfait discontinu quelconque, situé sur l'axe des θ. Soit M un point de P. Ajoutons à P son symétrique par rapport à M. Nous obtenons un ensemble parfait discontinu $P(M)$, symétrique par rapport à M. M est donc un point de seconde espèce (ou limite des deux côtés) de $P(M)$. Pour chacun des intervalles contigus i de $P(M)$ formons le rapport $l(i)$ des distances respectives à M de l'extrémité de i la plus éloignée et de l'extrémité de i la plus rapprochée de M.

$l(i)$ est borné indépendamment de i et de M, si la distance de i

à M surpasse un nombre donné. Quand i tend vers M, $l(i)$ possède une plus grande limite $\lambda(M)$ que nous appellerons *indice* de P en M. L'indice est un nombre au moins égal à 1 et peut être infini, même en tout point de P.

θ étant l'abscisse de M, l'indice $\lambda(M)$ peut encore être ainsi caractérisé (s'il est fini). Si petit que soit ε positif, il existe une suite de points $\theta + h_n$ situés sur P_1 tendant vers M et tels que, pour toute valeur de n, $1 < \left|\frac{h_n}{h_{n+1}}\right| < \lambda(M) + \varepsilon$. Il n'existe pas de suite analogue telle que $1 < \left|\frac{h_n}{h_{n+1}}\right| < \lambda(M) - \varepsilon$.

En tout point (sauf peut-être aux points extrêmes) d'une portion P_1 de P, l'indice de P_1 et celui de P coïncident.

Si P est épais, $\lambda(M) = 1$ en tous les points M où l'épaisseur de P est 1. Mais, même si P est épais en lui-même, l'indice $\lambda(M)$ peut être infini en certains points, et même en un ensemble dense de points de P.

On montre, selon un type de raisonnement maintes fois rencontré (voir par exemple, le Premier Théorème des nombres dérivés, Journal de Jordan, 1916) les propositions suivantes :

1. Si l'ensemble des points M où $\lambda(M) = \infty$ est partout dense sur P, cet ensemble est un résiduel de P. De même pour l'ensemble $\lambda(M) \geq \alpha > 1$.

2. Si P possède en chacun de ses points un indice fini, l'ensemble K des points de P au voisinage desquels cet indice est non borné, K est non dense sur P.

3. Si l'indice de P est en tout point inférieur à un nombre fixe $\alpha > 1$, il existe un nombre η positif et une portion P_1 de P, tels que, 1° si θ est quelconque sur P_1, 2° si θ' est quelconque à la fois sur P et dans l'intervalle $\theta - \eta$, $\theta + \eta$, il existe un nombre θ'' situé sur P et vérifiant les inégalités $1 < \left|\frac{\theta' - \theta}{\theta'' - \theta}\right| < \alpha$.

Car l'inexactitude de cette conclusion entraînerait sur un résiduel de P, l'inégalité $\lambda(M) \geq \alpha$.

La proposition précédente peut être appliquée à toute portion ϖ de P. Les portions P_1 pour lesquelles existe un nombre η sont donc partout denses sur P.

L'application de ces remarques à l'étude de $F(\theta)$ est immédiate. Il est évident qu'en tout point de P où l'indice est fini et autour duquel, sur P, $\psi(\theta)$ est borné, $\varphi(\theta)$ existe. Donc :

Si l'ensemble des points de P où l'indice de P est fini, est partout dense sur P, l'ensemble E_1 des points d'existence de $\varphi(\theta)$ est partout dense sur P.

Nous retrouvons comme cas particulier le théorème que l'ensemble E_1 des points d'existence de $\varphi(\theta)$ est partout dense sur tout ensemble épais, et en conséquence, que E, complémentaire de E_1, est de mesure nulle.

Si un ensemble parfait P possède en chacun de ses points un indice fini, l'ensemble des points où $\varphi(\theta)$ n'existe pas, ou est discontinue sur P, ou possède spécialement à P au moins un nombre dérivé infini, cet ensemble est non dense sur P.

De plus, l'ensemble des points où $\varphi(\theta)$ est dérivable spécialement à P et où sa dérivée spéciale à P est égale à $f(\theta)$, cet ensemble est partout dense sur P.

Comme exemple particulièrement simple d'ensemble dont l'indice est partout fini, nous citerons l'ensemble parfait classique de Cantor, obtenu en retranchant d'un segment continu l'intervalle occupant le tiers médian de ce segment, puis en recommençant l'opération sur chacun des deux segments conservés et en la répétant indéfiniment. $\lambda(M)$ est pour cet ensemble P_0 au plus égal à $\frac{5}{2}$ en tout point. Dans le cas le plus général, *il existe sur P_0 un ensemble fermé non dense K_0, tel que sur toute portion de P_0 sans points communs avec K, $F'(\theta) = \varphi(\theta)$ existe, est continue et douée spécialement à P_0 de nombres dérivés finis; de plus, en tous les points d'un ensemble partout dense sur P_0, $\varphi(\theta)$ admet $f(\theta)$ pour dérivée spéciale à P_0.*

Soit P un ensemble parfait quelconque, M un de ses points, θ l'abscisse de M, $P(M)$ l'ensemble parfait obtenu comme il a été dit plus haut.

Pour chaque intervalle i ou rs ($\theta < r < s$) contigu à $P(M)$ et pour lequel $l(i) > 2$ (on pourrait remplacer 2 par tout autre nombre indépendant supérieur à 1), formons le rapport $\frac{(s-\theta)^2}{r-\theta} = \mu(i)$ du carré de la distance à M de l'extrémité s de i la plus éloignée de M, à la distance à M de l'extrémité r de i la plus proche de M.

Il est aisé de voir que si la série $\mu(i)$ est convergente, il est possible de déterminer une suite $\theta + h_n$ située sur P et telle que la série $\frac{h^2_n}{h_{n+1}}$ soit convergente. La réciproque est évidente. Nous dirons que P est *normal* ou *anormal* en M selon que la série $\mu(i)$ relative à M est convergente ou divergente.

Toute portion de P contenant M entre ses extrémités est, en même temps que P, normale ou anormale en M.

On montre sans peine que, si un ensemble P est normal en chacun de ses points, il existe, si petit que soit le nombre positif donné s, un nombre positif η et une portion P_1 de P, tels que, pour toute valeur de θ située sur P_1 et quelque soit θ' sur P entre $\theta-\eta$ et $\theta+\eta$, il est possible de trouver une suite $\theta+h=\theta', \theta+h_1, \ldots,$ $\theta+h_n. \ldots$, de points situés sur P et tels que la série $\frac{h^2}{|h_1|}+\frac{h_1^2}{|h_2|}+$ $+\ldots+\frac{h_n^2}{|h_{n+1}|}+\ldots$ ait une somme inférieure à s.

De là résulte que, *si un ensemble parfait P est normal en chacun de ses points, l'ensemble des points de P où $\varphi(\theta)$ est non existante ou discontinue sur P, cet ensemble est non dense sur P.*

Considérons un ensemble parfait P dont la construction satisfait aux conditions suivantes. Soient $\beta_1, \beta_2, \ldots, \beta_n, \ldots$ une suite de nombres positifs inférieurs à $^1/_2$, et σ_0 un segment quelconque. A la première opération, nous retranchons de σ_0 un intervalle, de manière qu'il subsiste sur σ_0 deux segments σ_1 ayant chacun une longueur supérieure à $\beta_1\sigma_0$. A la seconde opération, nous extrayons de chaque segment σ_1 un intervalle, de façon que chacun des deux segments restants surpasse ce même segment σ_1 multiplié par $\beta_2 \ldots$ A la n^e fois, nous opérons sur 2^n segments σ_n conservés à la suite de l'opération précédente. De chacun de ces segments, extrayons un intervalle de manière que chacun des deux segments σ_{n+1} restants surpasse le segment σ_n d'où il est extrait, multiplié par β_n. Et ainsi indéfiniment.

1°. Si la plus petite limite de β_n pour n infini est positive, et égale à μ, P possède en chacun de ses points un indice au plus égal à $\alpha=\frac{1-\mu-\mu^2}{\mu-\mu^2}$.

2°. Si $\sigma_{n+1}=\sigma_n\beta_n$, P est normal ou anormal en chacun de ses points, selon que la série $\frac{\beta_1\,\beta_2\ldots\beta_n}{\beta_{n+1}}$ est convergente ou divergente.

Si donc $\beta_n=2^{-k^n}$, P est normal ou anormal selon que $k<2$ ou que $k\leq 2$.

L'ensemble E des points de non existence de $\varphi(\theta)$ est, nous l'avons vu, non dense sur le continu. Il se décompose en un ensemble non dense sur tout ensemble parfait (ou *clairsemé*) G_1 et un ensemble dense en lui-même G. Soit Π le dérivé de G. Π est parfait et G est partout dense sur Π. Π est anormal en tous les poins de G, sauf éventuellement en certains points formant un ensemble g non dense sur Π.

On peut montrer par des méthodes analogues aux précédentes, le résultat suivant.

Toute fonction $F(\theta)$ douée d'une dérivée seconde généralisée $f(\theta)$ (condition A) possède (indépendamment de la condition B) les propriétés ci-après :

L'ensemble E de non existence de la dérivée $F'(\theta) = \varphi(\theta)$ est non dense sur le continu. E est de mesure nulle. Les points où $\varphi(\theta)$ existe, sans posséder $f(\theta)$ pour dérivée exacte ou approximative, forment un ensemble de mesure nulle.

Sur tout ensemble dont P l'indice est en chaque point inférieur à 2, 1^0 *il existe une portion P_1 où $\varphi(\theta)$ existe, est continue, douée de nombres dérivés spéciaux à P finis,* 2^0 *$\varphi(\theta)$ admet en un ensemble de valeurs de θ partout dense sur P, la fonction $f(\theta)$ pour dérivée spéciale à P.*

Mathematics. — "*Ueber eineindeutige, stetige Transformationen von Flächen in sich*" (siebente Mitteilung [1]). By Prof. L. E. J. BROUWER.

(Communicated at the meeting of June 26, 1920).

Im folgenden gebe ich die Charakterisierung aller Klassen von eindeutigen stetigen Abbildungen einer beliebig vorgegebenen endlichfach zusammenhängenden Fläche μ auf eine beliebig vorgegebene, endlichfach zusammenhängende Fläche μ'.

Sei O ein Punkt von μ, F die Gruppe der geschlossenen stetigen Kurven von μ durch O (welche in bezug auf F nur dann als verschieden betrachtet werden, wenn sie sich nicht mittels stetiger Modifizierung unter Festhaltung von O ineinander überführen lassen), N eine „*Normalbasis*" von F, welche aus den, falls μ zweiseitig ist, der Fundamentalrelation

$$a_1 a_2 a_1^{-1} a_2^{-1} \ldots a_{n-1} a_n a_{n-1}^{-1} a_n^{-1} a_{n+1} \ldots a_{n+m} = 1$$

und, falls μ einseitig ist, der Fundamentalrelation

$$a_2^1 a_2^2 \ldots a_{n-1}^2 a_n^2 a_{n+1} \ldots a_{n+m} = 1$$

genügenden Kurven $a_1, a_2, \ldots a_{n+m}$ (die wir in dieser Reihenfolge

[1]) Vgl. diese Proceedings XI, S. 788; XII, S. 286; XIII, S. 767; XIV, S. 300; XV, S. 352; XXII, S. 811. Hinsichtlich der fünften dieser Mitteilungen kann bemerkt werden, dass der dortige Beweis auch unabhängig vom LÜROTH-CLEBSCHschen Theorem geführt werden kann, nämlich so: a.a.O. S. 357 Z. 21 wählen wir auf μ' eine solche einfache geschlossene Kurve k, welche ein alle Bildpunkte von Rändern und Verzweigungspunkten der g_ν sowie alle nirgends dichten Bilder von g_ν enthaltendes Gebiet g begrenzt, und ziehen $k+g$ stetig zusammen in einen Punkt P von g. Die durch diese stetige Kontraktion von $k+g$ bestimmte stetige Aenderung von α_e führt zu einer „*primitiven Abbildung α_l von μ auf μ'*", für welche die ausserhalb voneinander gelegenen Innengebiete G_ν einer endlichen Zahl einander nicht treffender einfacher geschlossener Kurven von μ je eineindeutig mit dem Grade ± 1 auf die punktierte Fläche μ' und der Rest von μ auf den Punkt P abgebildet wird. Sodann führen wir mittels wiederholter stetiger Verschmelzungen, jedesmal von einem durch α_l mit dem Grade $+1$ und einem durch α_l mit dem Grade -1 abgebildeten G_ν, α_l in eine „*homogen-primitive Abbildung α_q von μ auf μ'*" über, deren Gebiete G_ν entweder alle mit dem Grade $+1$ oder alle mit dem Grade -1 abgebildet werden. Dass alle homogen-primitiven Abbildungen n-ten Grades von μ auf μ' zur selben Klasse gehören, leuchtet unmittelbar ein.

In der sechsten Mitteilung ist S. 814 Fussnote [2]) *statt* Math. Annalen 81 *zu lesen* Math. Annalen 82.

geordnet denken) besteht, O' ein Punkt von μ', G die Gruppe der geschlossenen Kurven von μ' durch O', M eine Normalbasis von G, welche aus den Kurven $b_1, \ldots b_r$ besteht.

Zu einer eindeutigen stetigen Abbildung σ von μ auf μ', welche O in O', mithin jedes a_ν in ein Kurve a'_ν durch O' überführt, gehört ein „*Transformationsformelsystem*"

$$a'_\nu = \varphi_\nu (b_1 \ldots b_r) \; (\nu = 1, 2, \ldots n + m), \quad . \quad . \quad . \quad . \quad (1)$$

wo die φ Produkte darstellen.

Ist $\chi (b_1 \ldots b_r)$ ein willkürliches Element von G, so gehört das Formelsystem

$$a'_\nu = \chi \varphi_\nu \chi^{-1} \; (\nu = 1, 2, \ldots n + m), \quad . \quad . \quad . \quad . \quad (2)$$

welches wir zu (1) *ähnlich* nennen werden, ebenfalls zu O in O' überführenden Abbildungen von μ auf μ' als Transformationsformelsystem und zwar können diese *innerhalb der Klasse von* σ gewählt werden. Andererseits gehört zu jeder O in O' überführenden Abbildung von μ auf μ', welche zur Klasse von σ gehört, ein zu (1) ähnliches Transformationsformelsystem.

Somit bestimmt jede Klasse von Abbildungen von μ auf μ' (zu welcher ja immer O in O' überführende Abbildungen gehören) eine Menge von untereinander ähnlichen Transformationsformelsystemen. Diese Menge werden wir als das *formale Bild* der Klasse bezeichnen, so dass *unsere Aufgabe in der Ermittelung der Bedingungen besteht, unter denen zwei dasselbe formale Bild besitzende Abbildungsklassen von* μ *auf* μ' *identisch sind.*

Um die Lösung dieser Aufgabe formulieren zu können, konstruieren wir auf μ ein der Normalbasis N entsprechendes, in O zusammenhängendes *kanonisches Rückkehrschnittsystem* R, durch welches also μ in eine schlichte Fläche F, deren Grenze g in R liegt, dabei übrigens einzelne Segmente von R der Fundamentalrelation entsprechend zweimal durchlaufen kann, und m je von einem Flächenrande r_ν und einer zu R gehörigen, r_ν umschliessenden „Randschlinge" s_ν begrenzten Zylinderflächen $\zeta_\nu (\nu = 1, 2, \ldots m)$ zerlegt wird. Weiter wählen wir auf μ', im Falle dass diese Fläche eine projektive Ebene ist, eine gerade Linie l durch O' und auf l einen Umlaufssinn λ. Im Falle dass μ' eine projektive Ebene ist, werden wir sodann eine Abbildung eine *Normalabbildung* nennen, wenn sie jeden zu R gehörigen Rückkehrschnitt entweder in O' oder eineindeutig in l, und zwar das erste Mal, dass er in g auftritt, mit dem Umlaufssinne λ transformiert.

Die Lösung der gestellten Aufgabe gestaltet sich nunmehr folgendermassen:

Zu einem formalen Bilde B gehört nur eine einzige Klasse:

1°. *wenn die universelle Ueberlagerungsfläche von μ' offen ist.*

2°. *wenn die universelle Ueberlagerungsfläche von μ' geschlossen, μ aber offen ist.*

3°. *wenn μ' den Zusammenhang der projektiven Ebene besitzt, μ einseitig und geschlossen ist, wenigstens ein einseitiger Rückkehrschnitt von μ zweiseitig abgebildet wird und eine, mithin alle zu B gehörigen Abbildungen ungerade sind.*

Zu einem formalen Bilde B gehören zwei Klassen:

1°. *wenn μ' den Zusammenhang der Kugel besitzt und μ einseitig und geschlossen ist. Das entsprechende Kriterium besteht in der Parität der zugehörigen Abbildungen.*

2°. *wenn μ' den Zusammenhang der projektiven Ebene besitzt, μ zweiseitig und geschlossen ist und wenigstens ein Rückkehrschnitt von μ einseitig abgebildet wird. Das entsprechende Kriterium besteht in der Parität der auf der zweiseitigen Verdoppelung von μ' gemessenen Grade der zugehörigen Normalabbildungen.*

3°. *wenn μ' den Zusammenhang der projektiven Ebene besitzt, μ einseitig und geschlossen ist, wenigstens ein einseitiger Rückkehrschnitt von μ zweiseitig abgebildet wird und eine, mithin alle zu B gehörigen Abbildungen gerade sind. Das entsprechende Kriterium besteht in der Parität der auf der zweiseitigen Verdoppelung von μ' gemessenen Inhalte der zugehörigen Normalabbildungen.*

Zu einem formalen Bilde B gehören unendlichviele Klassen:

1°. *wenn μ' den Zusammenhang der Kugel besitzt und μ zweiseitig und geschlossen ist. Das entsprechende Kriterium besteht im Grade der zugehörigen Abbildungen.*

2°. *wenn μ' den Zusammenhang der projektiven Ebene besitzt, μ zweiseitig und geschlossen ist und alle Rückkehrschnitte von μ zweiseitig abgebildet werden. Das entsprechende Kriterium besteht im absoluten Werte des zugehörigen auf der zweiseitigen Verdoppelung von μ' gemessenen Abbildungsgrades.*

3°. *wenn μ' den Zusammenhang der projektiven Ebene besitzt, μ einseitig und geschlossen ist und alle einseitigen Rückkehrschnitte von μ einseitig abgebildet werden. Das entsprechende Kriterium besteht im absoluten Werte der Grade der zugehörigen Abbildungen der zweiseitigen Verdoppelung von μ auf die zweiseitige Verdoppelung von μ'.*

Kryo-Biology. — "*Einwirkung sehr niederer Temperaturen auf die Moosfauna*". By P. GILBERT RAHM (at Maria Laach). (Versuche im physikalischem Laboratorium der Universität Leiden und der kryologisch-biologischen Versuchsstation des Niederländischen Kälte-Vereins, Leiden Communications Suppl. N°. 43*b*). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of June 26, 1920).

Als „Moosfauna" im allgemeinen bezeichne ich nach dem Vorschlag FR. HEINIS (cf. „Systematik und Biologie der moosbewohnenden Rhizopoden, Rotatorien und Tardigraden der Umgebung von Basel mit Berücksichtigung der übrigen Schweiz". Archiv für Hydrobiologie und Planktonkunde. Stuttgart 1910. Bd. V. Heft 2, p. 91) „die Gesamtheit der in den Moos = resp. Flechtenrasen vorkommenden Tiere". Diese Definition umfasst sowohl die:

I. *Bryophilen Formen,* d.h. solche, die in den Moosrasen „ihre Existenzbedingung" finden. [cf. RICHTERS, F. Die Fauna der Moosrasen des Gaussberges und einiger südlicher Inseln". Deutsche Südpolar-Expedition 1901—1903, Berlin 1907. (Zoologie), p. 292]. Ihre Nahrung können die lebende Moospflanze, organischer Detritus, und andere Tiere sein. [cf. HEINIS l.c.p. 91].

II. *Bryoxene Formen,* d. h. solche, die entweder nur während einer bestimmten Entwicklungsperiode im Moose leben oder zufällig im Moosrasen gefunden werden.

Zur *ersten* Gruppe gehören Protozoen, Rotatorien, Nematoden, Tardigraden und Gamasiden.

Zur *zweiten* Gruppe rechnet HEINIS [l.c. p. 91]. Larven von Lauf- und Rüsselkäfern, Fliegenlarven, Myriopoden, Arachniden, Mollusken etc.

In der folgenden Arbeit findet der Hauptsache nach nur die Moosfauna im engeren Sinne Berücksichtigung, vor allem die Gruppen der *Tardigraden* (Bärtierchen), *Nematoden* (Fadenwürmer), und *Rotatorien* (Rädertierchen).

Da diese Tiere in grossen Mengen die Moosrasen der kalten Zone bewohnen, müssen sie auch eine grosse Anpassungsfähigkeit an niedere Temperaturen besitzen.

Prof. F. Richters, der berühmte Altmeister der Moosfauna, untersuchte Bryum-Rasen vom Gaussberg, in dem — 41° C. gemessen wurde. [Richters l.c.] Ueberhaupt scheinen die Moose der kälteren Gegenden das Dorado der Moosfauna zu sein, während die Tropen nach den Angaben Murrays und Richters relativ arm an Moosbewohnern im engeren Sinne sind.

Von diesem Gesichtspunkte ausgehend stellte ich im Oktober und November 1919 im chemischen und physikalischen Institut der Bonner Universität mit Tieren der oben genannten Moosfauna einige Temperaturversuche an. Eine kurze Zusammenfassung der Ergebnisse ist in den Sitzungsberichten der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn 1920 (1919) p. 21—23 veröffentlicht.

Es zeigte sich, dass verschiedene Gruppen von Tieren, die die Fähigkeit besitzen, mit den Moosen auszutrocknen und nach dem Anfeuchten des Mooses wiederaufzuleben, im trockenen sogenannten asphyktischen Zustand sehr tiefe Temperaturen ertragen können. Temperaturen von *c.* — 183° *C.*, die mittels flüssiger Luft erzielt wurden, überstanden die Versuchstiere, Tardigraden, Rotatorien und verschiedene Arten von Nematoden *schadlos* 26 *Stunden lang.*

Da ich in Bonn keine Gelegenheit hatte, noch tiefere Temperaturen herzustellen, wandte ich mich an den Leiter des Kryogenen Instituts, Herrn Prof. Dr. Kamerlingh Onnes, mit der Bitte, mir zu gestatten, in seinem weltberühmten Institut einige Versuche mit flüssigem Wasserstoff, wenn möglich auch mit flüssigem Helium, ausführen zu dürfen. Herr Prof. Dr. Kamerlingh Onnes schrieb mir gütigst zurück, dass mir so viel flüssiger Wasserstoff zur Verfügung stehe, als ich zu meinen Versuchen benötige. Ich erhielt sogar die freundliche Zusage, mit flüssigem Helium arbeiten zu dürfen, falls nach den Versuchen mit lüssigem Wasserstoff sich dazu die Notwendigkeit ergebe.

I. Versuch mit flüssiger Luft.

Da ich in Leiden auch über beliebige Mengen flüssiger Luft verfügen konnte, bat ich den Conservator des kryogenen Instituts, Herrn Dr. Crommelin, zunächst einen Versuch mit flüssiger Luft der sich auf einige Tage erstrecken sollte, ausführen zu dürfen. Die Moosproben wurden in leichtes Papier eingehüllt in einem Gazebeutel, der mittels einer Bleikugel beschwert war, sofort in ein bereitstehendes Bad von flüssiger Luft getaucht. Die Tiere befanden sich in den lufttrockenen Moosen im asphyktischen Zustand. *Der Versuch dauerte* 125 *Stunden.*

Nach dem Wiederanfeuchten bald nach dem Versuch erwachten fast sämtliche Tiere in verhältnismässig kurzer Zeit. Die folgende Tabelle soll eine Uebersicht über die Versuchstiere, die Dauer ihres Trockenschlafes und die Zeit ihres Wiederaufwachens geben.

TABELLE I.

Bad in flüssiger Luft.
Dauer: 125 Stunden.
Zeit: 11. II. 1920 bis 16. II. 1920.
Temperatur: c. —190° C.

Moosart.	Wiedererwachen.			
	Trocken-schlaf.	Rotatorien.	Tardigraden.	Nematoden.
A. Grimmia spec. von einem Strohdach aus Amerongen.	8 Tage.	Adineta barbata Jans. Die I. in 16 Min.	Macrobiotus Hufelandi C. Schultze. Der I in 19 Minuten, andere in 32 M.	Plectus rhizophilus De Man. Der I. juv. in 33 Minuten, sen. in 46 Minuten.
B. Tortula ruralis Ehrh. von einer Gartenmauer aus Honnef a. Rhein.	16 Tage.	Callidina constricta Duj. Die I. in 5 Minuten.		
C. Racomitrium spec. bei Scheveningen an den Dünen.	5 Tage.	Gen.? spec.? Das I. in c. 20 Minuten.		Plectus parietinus Bast. Der I. in 70 Minuten.

Wurden die Moosproben nach dem Kälteexperiment längere Zeit aufbewahrt, ehe sie angefeuchtet wurden, so erwachten die Tiere gewöhnlich etwas später. Eine allgemeine für alle Tierarten gültige Regel liess sich mit Sicherheit noch nicht ableiten. 3 Monate später wurde z. *B* eine Probe von *A* untersucht und nach dem Wiederanfeuchten erwachte ein Rotator fast genau zu der in Tabelle I angegebenen Zeit, eher noch ein bis 2 Minuten früher. Die Rotatorien von *C* brauchten indes volle 2 Stunden, bis sie nach dreimonatlichem Trockenschlaf ihre volle Lebenstätigkeit wiedererlangten. 2 Echinicus-Arten (gepanzerte Tardigraden) erwachten nach mehr als dreimonatlichem Trockenschlaf in *B* nicht mehr. Die Kälte hierfür verantwortlich zu machen, scheint mehr als fraglich, wie aus spätern Versuchen klar hervorgeht. Eher könnte man sagen, dass diese Tiere schon vorher durch das Austrocknen geschädigt wurden. Denn die Fähigkeit der Versuchstiere wiederholt auszutrocknen und wiederaufzuwachen, ist nicht unbegrenzt.

II. Versuch mit flüssigem Wasserstoff.

TABELLE II.

Dauer: 26 Stunden.
Zeit: 11. II. bis 12. II. 1920.
Temperatur: —253° C.

Moose.	Trocken-schlaf.	Wiedererwachen.		
		Rotatorien.	Tardigraden.	Nematoden.
A. wie I.	8 Tage.	Adineta barbata Jans. in c. 15–20 Minuten.	Macrobiotus Hufelandi C. Schultze in 20 Minuten.	Plectus rhizophilus De Man 25 Minuten.
B. wie I.	16 Tage.	Callidina constricta Duj. in 3 Minuten.		
C. wie I.	5 Tage.	In 18 Minuten ein Rotifer spec.? Callidina brauchten mehr.		

Vergleicht man Tabelle I und II, so findet man kaum bedeutende Unterschiede. Als Regel scheint festzustehen, dass Rotatorien am schnellsten nach dem Wiederanfeuchten zum Leben zurückkehren; es folgen die Tardigraden und zuletzt die Nematoden. Ferner scheint ein ganz kurzer Trockenschlaf mit folgendem kalten Bad auf das Wiedererwachen verzögernd zu wirken. Man vergleiche z. *B* das über Rotatorien Gesagte in Tabelle I und II.

III. *Versuch mit flüssigem Helium.*

Da Herr Prof. Dr. Kamerlingh Onnes durch Krankheit verhindert war, während meines Aufenthaltes in Leiden flüssiges Helium herzustellen, bat ich Herrn Conservator Dr. Crommelin, die Versuche für mich auszuführen, sobald sich eine Gelegenheit dazu biete. Herr Prof. Dr. Kamerlingh Onnes besass die grosse Freundlichkeit, die Versuche selber zu leiten. Die Moose wurden dann sofort nach dem kalten Bad mir zur Untersuchung nach Bonn gesandt.

Dem Briefe des Herrn Prof. Dr. Kamerlingh Onnes vom 16. III. 1920 entnehme ich folgendes:

„Am 10. III 1920 12^{u} wurden die Moose lufttrocken in den Helium-Apparat gebracht. Dieser wurde dann — was für die Heliumverflüssigung nötig ist — luftleer gepumpt, blieb 24 Stunden luftleer bei gewöhnlicher Temperatur stehen, wurde sodann mit Heliumgas

bei gewohnlicher Temperatur gefüllt und langsam 2 Grad pro Minute abgekühlt bis —150° C. Es wurde sodann das Präparat mit flüssigem Helium überschüttet und blieb in demselben von 1^u bis 8^u, 45^m. Während 2 Stunden wurde die Temperatur auf 1°,22 K erniedrigt".

TABELLE III.

Dauer: $7^3/_4$ Stunden vgl. auch das im vorigen Abschnitt Gesagte.
Zeit: 10. III — 11. III im Vacuum, 11. III 12^h — 8^h, 45^m im flüssigen Helium.
Temperatur: — 269° C bis — 271,88° C.

1. Für Moos B. erste Untersuchung 21. III. 1920.

Tag der Untersuchung.	Wiedererwachen.		
	Rotatorien.	Tardigraden.	Bemerkungen.
21. III. 1920.	1. Callidina nach 91 Minuten.	Echiniscus trifilis (neue Art) sen. nach 23 Min. juv. „ 31 „	Nach 8 Stunden waren fast alle Tiere munter.
24. III. 1920.	Alle lebend.	Fast alle lebend.	
26. III. 1920.	„ „	7 noch lebend.	
28. III. 1920.	„ „	Einige schlüpften aus den Eiern.	
7. IV. 1920.	„ „	Zahl d. lebenden Tiere nimmt ab.	
12. IV. 1920.	„ „	Nur einer lebend.	
14. IV. 1920.	Einige lebten.	Alle tot.	

2. Für Moos B zweite Untersuchung.
Am 28. IV. 1920. 10^h,45^m morgens eine neue Probe angefeuchtet.

Tag der Untersuchung.	Wiedererwachen.	
	Echiniscus trifilis n. spec.	Milnesium tardigradum Doy.
28. IV. 1920. 10^h,45^m.	In einer Stunde war der erste alte Echiniscus erwacht; es folgte einer von mittlerer Grösse.	Nach einer Stunde und 13 Minuten erste Bewegung.
29. IV. 10^h morgens	Noch ein alter munter.	sehr lebhaft.
29. IV. 2^h,5^m.	Auch ein junger erwacht.	„ „
29. IV. 5^h.	Viele alte und junge erwacht.	„ „

Dann alles von neuem eintrocknen lassen.

Tag der Untersuchung	Wiedererwachen.	
	Echiniscus trifilis non spec.	Milnesium tardigradum.
4. V. 11h,2m morgens.	Bis 6. V. nichts mehr erwacht.	
6. V. 4h,47m.	Ein junger aus dem Ei geschlüpft	
7. V.	Alles tot.	Alles tot.

Parallelversuch, um zu prüfen, ob die Schäden beim Wiedereintrocknen nach dem kalten Bad auf das Kälteexperiment zurückzuführen sind oder ob die Versuchstiere überhaupt ein mehrmaliges Wiedereintrocknen nicht schadlos ertragen können.

Denis Lance schreibt in seinen Thèses présentées à la Faculté des sciences de Paris pour obtenir le grade de docteur des sciences naturelles, Paris 1896, „9 bis 14 mal kann man die Tiere — gemeint sind Bärentierchen (Macrobioten) — austrocknen lassen. Die Zeit, die zur Wiederaufnahme der Lebenstätigkeit erforderlich ist, wächst mit der Zahl der Austrocknungen". Ich muss gestehen, dass es mir noch nie gelang, Tardigraden spec. Echiniscus-Arten öfters als 5 bis 7 Mal auszutrocknen. Freilich hängt es auch ganz von dem Grad und der Dauer der Austrocknung ab. Macrobioten ertragen mehr als die gepanzerten Echiniscus-Arten. Rotatorien sind am widerstandsfähigsten.

TABELLE IV.

Parallelversuch mit Moos B, das nur lufttrocken seit 23. I. 1920 aufbewahrt worden war.

Tag der Untersuchung und Stunde d. Anfeuchten.	Wiedererwachen.		
	Callidina spec.?	Milnesium tardigradum Doy.	Echiniscus trifilis.
7. V. 1920. 4h,49m.	5h, 14m, also in 25 Minut.		5h, 14m, also in 25 Minut.
7. V. 1920. 5h,41m.	6h, 00m, also in 19 Minut.	6h, 13m, also in 32 Minut.	6h, 03m, also in 22 Minut.
Dann alles eintrocknen lassen. 8. V. 8h abends trocken.			
10. V. 1920. 9,24h morgens.	9,50h 3 junge schon sehr munter.	c. 1/4 11h erwacht.	Nur einer 9,50h mittelgross, alle andern schienen tot.

Alles eintrocknen lassen. 11. V. 11h abends alles trocken.

14. V. 1920. 8,35h morgens.	9,13h d. erste. 9,15h 3 Stück.	c. 9,30h.	10h abends war einer aus dem Ei geschlüpft.
15. V. 1920. 8h morgens.	Alle lebhaft.	Sehr munter.	Auch ein grösserer erwacht, ein alter bewegte sich auf Anstoss mit der Pinzette.

Alles eintrocknen lassen. 16. V. mittags trocken.

17. V. 1920. 8,35h morgens.	8,50h eine erwacht.	tot?	Alle scheinen tot.
11,30h morgens.	sehr lebhaft.	tot.	Ein erwachsener u. ein kleiner munter.

Vergleicht man die Tabellen mit einander, so wird man wohl sagen dürfen, dass das kalte Bad (besser wohl die durch das kalte Bad bewirkte Austrocknung) den Echiniscus Arten schädlich war. [1])

TABELLE V.

Bad in flüssigem Helium mit Moosart C. Allgemeine Bemerkungen s. p. 4—5.

Erste Untersuchung.

Dauer: s. p. 4—5.
Zeit: s. p. 4—5.
Temperatur: s. p. 4—5.

Tag d. Untersuchung u. d. Anfeuchtens.	Rotator Callidina.	Macrobiotus Hufelandi.	Nematode Plectus parietinus.
21. III. 10,52h morgens.	11,37h, also in 45 M.		11,49h, also in 58 Min. 12,10h ein junger.
22. III. 10,30h morgens.	sehr munter.	Einer war sehr munter. Zeit des Erwachens unbestimt.	lebhaft.

In der folgenden Tabelle soll die Lebensdauer der einzelnen in Tabelle V angeführten Tiere verfolgt werden.

[1]) *Anmerkung*: Nach der Drucklegung wurden die in Tabelle IV mitgeteilten Untersuchungen fortgesetzt. Ich liefs die Tiere noch zweimal eintrocknen. Echiniscen und Rotatorien erwachten auch noch nach der letzten, also 6 Austrocknungspeririode. Die Versuche werden fortgesetzt.

Datum.	Callidina.	Macrobiotus.	Plectus.	Bemerkungen.
22. III.	Sehr munter 2 Stück.	Stirbt am Abend.	2 kleine sehr munter.	Es erscheinen in der Schale Protozoen von ganz charakteristischer Gestalt, die ich noch in keinem anderen Moos beobachtet habe. Die Tiere schwimmen lebhaft umher. Ob nachträglich hineingekommen, bleibt fraglich. Mehrere Milben erwachten nicht mehr.
24. III.	» »		» »	
26. III.	» »		» » Ein grosser Plectus parietinus Bast 0,6 mm gross doch nicht geschlechtsreif. Bei der Bestimmung leider getötet.	
27. III.	» »		Ein junger noch lebhaft.	
28. III.	» »			
29. III.			2 Nematoden sehr lebendig.	Viele Protozoen.
30. III.	Einer lebhaft.			
1—8. IV.	» »		» »	Protozoen nehmen ab.
9. IV.	Einer sehr lebhaft.	Sehr munter, wohl geschlüpft.	2 sehr lebhaft.	Junger Echiniscus trifilis lebte, starb aber bald nach Überführung in ein bes. Gefäss.
10. IV.	» »	lebt noch	Nur einer noch lebhaft.	
11. IV.			Nur auf Anstoss hin erfolgt Bewegung des Kopfes.	
14. IV.	tot.	tot.	tot.	Viele kleine Protozoen.

Zweite Untersuchung v. Moos C.

Tag der Untersuchung bzw. des Anfeuchtens.	Rotatorien. Callidina. spec.?	Nematoden. Plectus parietinus.	Bemerkungen.
29. IV. 8,45h morgens.	9,53h eine sehr lebhaft.	Nur ein junger erwachte, 2 alte erwachten bis 10 V. nicht mehr.	Die merkwürdigen Protozoen s. oben erscheinen wieder, also doch nicht nachträglich hineingekommen.

IV. *Versuch. Bad in flüssigem Wasserstoff.*

Um zu erproben, wie die Versuchstiere sich verhalten, wenn sie bereits völlig aus dem Trockenschlaf erwacht und im Wasser ihre Bewegungen aufgenommen haben und dann einfrieren, wurden bereits im verflossenen Winter im Bonner Chemischen Institut Versuche angestellt. Eine Kältemischung von —81° C., die mehrere Stunden einwirkte, überstanden bei langsamen Einfrieren fast alle Versuchstiere. Selbst die Kälte der flüssigen Luft schadete den Tieren nicht, wenn man die Kälte anfangs langsam einwirken liess [1]). Liess man aber das Wasser, in dem sich die Tiere befanden, plötzlich einfrieren, so war der Prozentsatz der Tiere, die nach dem Auftauen lebten, sehr gering. Im Kryogenen Institut der Universität Leiden wurden folgende Versuche ausgeführt:

1. 2 Moosproben „wurden zuerst *angefeuchtet* und eingewickelt in ein bischen Gaze und am 20. März 1920 von 10^h bis 4^h *langsam abgekühlt* im Dampf von flüssiger Luft. Sodann wurden sie eingetaucht in flüssige Luft. Sie blieben darin bis 12. März 11^h. (Also c. 2 Tage). Dann wurden sie aus der flüssigen Luft genommen und gleich in flüssigen Wasserstoff gebracht und blieben hierin bis 13. März 10^h, 30^m. (Also c. 1 Tag). Darnach sind sie schnell auf gewöhnliche Temperatur gekommen". Aus dem Brief des Herrn Prof. Dr. Kamerlingh Onnes an mich vom 16. III. 1920.

Herrn Dr. Drooglever Fortuyn hatte ich vor meiner Abreise aus Leiden gebeten, einen Teil dieser Proben nach dem Auftauen an Ort und Stelle zu untersuchen. Er hatte die grosse Freundlichkeit, mir über das Ergebnis am 13. III. 1920 zu berichten. „In der langsam abgekühlten Probe belebte sich schon nach 12 Minuten ein Nematode, welcher kräftige Bewegungen machte. Nach 20 Minuten belebte sich der erste Tardigrade, bald von vielen andern gefolgt".

Die Proben wurden mir dann lufttrocken zugesandt. Das Ergebnis der Untersuchung sei in folgender Tabelle mitgeteilt.

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[1]) *Anmerkung:* Liess man die Tiere im Wasser nochmals einfrieren, so waren die meisten nach dem Auftauen tot. Also hatte das kalte Bad doch die Widerstandskraft geschädigt. Es überstanden nur Rotatorien. Es kam bei diesem Versuch nur die Kältemischung von —81° C. zur Verwendung.

TABELLE VI.

Moosprobe A.

Dauer: 1 Tag in fl. Wasserstoff, 2 Tage fl. Luft.
Zeit: 10. III. 1920 bis 13 III. 1920.
Temperatur: — 253° C. bzw. — 192° C.

Tag der Untersuchung.	Callidina russeola Zel.	Macrobiotus Hufelandi.	Milnesium tardigradum.	Plectus rhizophilus.	Bemerkungen.
24. III. 5,35h abends.	5,45h also in 10 Minuten mittelgross.	6,20h ziemlich lebhaft dunkel pigmentiert.	2 Stück noch schlafend.		
10,05h abends	sehr lebhaft schwimmend.	Einer am Erwachen, auch dunkel pigmentiert.	Einer bewegte sich auf Anstoss.	Noch schlafend.	
25. III. 9,45h morgens.	2—3 sehr lebhaft.	Nur einer noch lebhaft.	» »	2 junge lebhaft.	
27. III. 11,25h morgens.	» »	» »		Älterer erwacht.	
28. III.	» »	» »		sehr lebhaft.	
29. III. 8h morgens	» »	tot.	tot.	2 kleine lebhaft.	Protozoen treten auf.
10h abends.	» »	Ein kleiner, wohl geschlüpft.		» »	
30. III. 1h mittags.	» »	Ein alter nimmt die Bewegung wieder auf.		» »	
6h abends.	» »	Alter tot.		» »	
31. III.	» »			Dazu ein alter.	
1—7. IV.	» »			alle lebhaft	
7. IV. 3,15h mittags.	» »	Ein alter lebhaft.		» »	
8. IV.	» »	» » »			
9. IV. 9h morgens.	» »	Auch kleiner, wohl geschlüpft.			
10. IV. 9,15 abends.	» »	Der kleine sehr lebhaft.		alter sehr munter.	
11. IV.	» »	» »		» »	
12. IV.	» »	» »		» »	
14. IV.	» »	» »		» »	

Tag der Untersuchung.	Rotator.	Macrobioten.	Nematoden.	Bemerkungen.
26. IV.	mehrere sehr lebhaft.	3 kleine, wohl geschlüpft.	Der alte sehr munter.	
28. IV.	„ „	3 sehr munter.	„ „	
1 V. 11,30h morgens.	„ „	„ „	Dazu noch 2 jüngere.	
3. V.	„ „	„ „	„ „	
6. V.	„ „		Nur einen lebhaft gesehen.	
8. V. 8,55h morgens.	„ „	Einer sehr munter Macrob. echinogenitus Richters.	Einer lebhaft.	
9,40h morgens.	„ „		3 ziemlich erwachsen, munter.	Eine lebende Milbe, wohl nachträglich hineingekommen oder geschlüpft??
10. V.	„ „	ein erwachsener Hufelandi lebhaft.	Ein grosser bewegte sich nur auf Anstoss.	
12. V.	träge Bewegungen auf Anstoss.	Ein Hufelandi mittelgross, dunkel, lebhaft,	Alle tot	
14. V.	Alles schien tot.			

Moosprobe A. 2. Untersuchung.

Tag der Untersuchung.	Rotator.	Macrobiotus.	Nematoden.
5. V. 5,40h abends.	9,40h 2 kleine sehr lebhaft, wohl lange vorher erwacht.	6,30h ein Hufelandi lebhaft.	9,40h. Einer bewegte sich ein wenig.
6. V. 8,30h morgens.	sehr lebhaft.	noch einer erwacht.	
7. V. 8h morgens.	schien alles tot.		

Moosprobe B. desselben Versuchs.

Datum des Anfeuchtens und der Untersuchung.	Rotatorien. Callidina.	Echiniscus trifilis non spec.	Bemerkungen.
24. III. 5,38h abends.	9,55h erste am Erwachen. 10h mehrere lebhaft.		

Datum der Untersuchung.	Rotatorien.	Echiniscus.	Bemerkungen.
25. III. 1920.	lebhaft.	alle tot.	
27. III. bis 30. III.	„		
31. III. 10h morgens.	„	Einer schlüpft aus dem Ei.	Viele Protozoen erscheinen.
1. IV. bis 14. IV.	„	starb bald.	
14 IV. 10,20h morgens.	„	Einer geschlüpft, 0,150 mm. gross.	Protozoen vermehren sich sehr stark.

Die Eier der Echinisci scheinen also bei weitem widerstandsfähiger zu sein wie die Tiere selbst. Es erwachte überhaupt kein erwachsener Echiniscus.

2. Ein *zweiter* Versuch wurde mit Moosproben gemacht, die *vorher angefeuchtet* und dann *plötzlich in flüssige Luft und in flüssigen Wasserstoff* getaucht wurden. Herr Prof. Dr. Kamerlingh Onnes schrieb mir darüber am 13 III 1920: „Diese Probe wurde zuerst angefeuchtet und in Gaze eingewickelt und sodann 10 März 11h plötzlich in flüssige Luft gebracht und blieb darin bis 12 März 11h (also 2 volle Tage). Sodann wurde sie wie die vorige in flüssigen Wasserstoff getaucht und blieb darin bis 13 III. 10h,30" (also fast einen Tag.).

Herr Dr. Droogleever Fortuyn untersuchte auch von dieser Probe gleich nach dem Auftauen einen Teil und fand alles tot „wenigstens war nach 2 Stunden und 20 Minuten keine Bewegung sichtbar". Brief vom 13 III, 1920.

Der übrige Teil der Probe wurde mir dann lufttrocken zugesandt. Das Ergebnis einer genaueren und längeren Untersuchung sei in folgender Tabelle mitgeteilt: p. 511.

Von den Moosproben *waren A und B zusammengeschüttet worden.* In einem andern Gefäss derselben Probe, die auch am 24. III angefeuchtet war, bemerkte ich erst am 8. IV eine Adineta lebhaft umherschwimmend. Vielleicht war das Tier inzwischen geschlüpft. Es lebte noch am 6. V. An diesem Tage bemerkte ich noch einen Rotifer lebhaft umherschwimmend [1]).

Auf meine Anfrage hin teilte mir Herr Conservator Dr. Crommelin mit, dass die Moose 1 bis $1^1/_2$ Stunden vor dem Kälte-experiment

[1]) *Anmerkung:* Rotatorien lebten noch am 25. IX. 1920. Aus den Eiern schlüpften viele Macrobioten.

angefeuchtet wurden. Es ist also wohl ausgeschlossen anzunehmen, dass sich Callidina russeola Zel. beim Einfrieren noch im asphyktischen Zustand befand. Am 27. V waren sehr viele Rotatorien und einige Macrobioten geschlüpft.

TABELLE VII.

Dauer: 3 Tage.
Zeit: 10. III. 1920 bis 13. III. 1920.
Temperatur: — 253° C. bezw. — 192° C. s. vorher.

Datum der Untersuchung.	Rotatorien.	Bemerkungen.
24. III. 10,55h morgens.	Erst 4,55h eine grosse Callidina russeola Zel. am Erwachen.	Viele tote Echiniscen, Macrobioten, Rotatorien und Nematoden.
10,15h abends.	sehr lebhaft, sich ausstreckend und schwimmend.	
25. III. bis 15. IV.	Meist sehr lebhaft, nur abends in Ruhe.	
16. IV. 9h abends.	Bewegt sich nur auf Anstoss.	
25. IV.	Nur langsame träge Bewegungen.	
27. IV.	Bewegungen sehr träge.	
28. IV.	" " "	Das Tier war am Schlusse ziemlich abgemagert, obwohl ihm Detritus zur Verfügung stand.
29. IV.	reagiert kaum noch.	
1. V.	tot.	

Also ist kaum eine Schädigung durch das kalte Bad festzustellen. Die Tiere leben auch sonst nicht länger.

Zusammenfassung der bisherigen Ergebnisse.

I. Die Tiere der Moosrasen können im asphyktischen Zustand Temperaturen von — 271,8° C. mehrere Stunden ertragen. (Tardigraden, Nematoden und Rotatorien). Protozoen scheinen auch diese Temperaturen zu überstehen, bedürfen aber noch einer sorgfältigen Nachprüfung. Temperaturen von — 192° C. wurden 5 Tage lang schadlos ertragen. Auch die Eier dieser Tiere werden nicht geschädigt.

II. Ein ganz kurzer Trockenschlaf mit folgendem kalten Bad scheint auf das Wiedererwachen verzögernd zu wirken.

III. Am schnellsten erwachen Rotatorien; es folgen die Tardigraden und zuletzt die Nematoden.

IV. Durch die Kälte scheint die Fähigkeit der Echiniscus Arten, öftere Austrocknungsperioden zu überstehen, gemindert zu werden.

V. Lässt man die Tiere im wachen Zustand in Wasser langsam einfrieren, so ertragen die meisten die Temperatur — 253° C. 24 Stunden schadlos. Eine Ausnahme scheinen die Echiniscen zu machen.

VI. Lässt man die Tiere im wachen Zustand in Wasser plötzlich einfrieren, so sterben die meisten in extremer Kälte. Nur Rotatorien können schadlos überstehen und die Eier der Macrobioten.

VII. Handelt es sich in den ersten Fällen, wo die Tiere im asphyktischen Zustand die tiefen Temperaturen ertragen, nur um eine Schädigung der Kälte als Wasserentziehung, die dem Austrocknen gleichkommt, (s. Pütter, vergleichende Physiologie, Jena 1911, p. 385), so liegen die beiden zuletzt berichteten Fälle N°. V u. VI, doch wesentlich anders. Hier könnte auch noch eine „mechanische Zertrümmerung der Plasmastruktur" in Betracht kommen.

Wirkt die Kälte langsam ein, so wäre es vielleicht möglich daran zu denken, dass die Kälte als Reiz wirkt, (sowie die beginnende Austrocknung des Mooses) in den asphyktischen Zustand überzugehen. Bei Fall VI scheint indes diese Erklärung nicht zuzutreffen.

Zum Schluss habe ich allen Herrn vom Kryogenen Institut zu danken, die am Zustandekommen der Versuche mitwirkten. In erster Linie herzl. Dank dem Leiter des Instituts, Herrn Prof. Dr. Kamerlingh Onnes, der meinen Arbeiten so grosses Interesse entgegenbrachte und mir so grosses Entgegenkommen bewies. Herzlichen Dank auch dem Herrn Conservator Dr. Crommelin, Herrn Dr. Droogleever Fortuyn, die mich mit Rat und Tat unterstützten, nicht zu vergessen Herr Mechaniker Flim, der das Material bereitwilligst herstellte, und Herr Stud. Delhez, der mir beim Untersuchen half.

Chemistry. — "*The velocity of the diazotisation reaction as a contribution to the problem of substitution in the benzene nucleus.*" By Prof. J. BÖESEKEN, W. F. BRANDSMA and H. A. J. SCHOUTISSEN.

(Communicated at the meeting of February 28, 1920).

1. In regard to the problem of the substitution in benzene, the question has been considered whether only the group already present is decisive as to the place where the group newly introduced is to come or whether the nature of that new group too plays an important part.

Supposing the last alternative to be right, one of us [1]) has projected the following scheme of the subsequent stages during the substitution, by which at the same time the answer was given to the question why in one case meta-, in another case para- and ortho-derivatives are formed by preference.

If the acting molecule has an inclination to combine with group X of the benzene derivative C_6H_5X, then two courses may be taken:

a. The acting molecule combines or reacts with this group; then no substitution in the nucleus takes place.

b. The acting molecule has some inclination to combine with group X, which inclination however only tends to effect a shifting of affinity (electrones). In this case a change of condition will take place in the benzene nucleus, designated by him as a "chinoid shifting of the affinities", and which consists of an accumulation of attraction at the para and at one of the ortho places.

If the acting molecule has no inclination to combine with group X, then no preference will be shown for ortho- and para-substitution and substitution of the meta H-atoms is sooner to be expected.

The stress in these considerations is therefore laid on the affinity between the molecule to be introduced and the group already present; an experimental illustration and eventually a comfirmation of this theory may be expected, if quantitative data can be acquired on this reciprocal effect. When e.g. we could determine the rate of

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[1]) BÖESEKEN: Koolwaterstoffen II, (Hydrocarbons II, edited by WALTMAN, Delft) page 125—127 and 134—137. See also these Proc. of March 30, 1912.

eraction of an entering molecule with group X, then one could immediately trace the influence on this reaction velocity of the situation and of the nature of different groups in the benzene nucleus.

If e.g. a group X directs substituents to the para- and ortho-place, it is to be expected that the rate of reaction mentioned above will be the most modified by groups already present in the ortho- or para-position and less by groups in the meta-position.

If on the other hand we had a group X directing to the meta place, then the reverse would have to be expected if for the rest the acting molecule and the circumstances are the same.

To this end we have in the first place selected the diazotisation reaction, viz. the rate of reaction of the NH_2 group with HNO_2, partly as the NH_2 group directs to para and ortho in a very pronounced way, partly because HNO_2 will show a great similarity in its nature with HNO_3, the reagent examined most fully by HOLLEMAN and his pupils.

In this case one will have to take into consideration that the velocity of the diazotisation may also depend on the basicity of the amine. For instance it is not at all out of the question that the reaction exclusively takes place between the free amine and free nitrous acid. Then this reaction will be the quickest with the weakest bases because their salts are hydrolysed in the highest degree. Now if the meta substituted amines are stronger bases than the para- and ortho-substituted ones, then the first mentioned would show a smaller rate of diazotisation than the last. As however the basicity can be deduced from data independent of the rate of diazotisation, its influence can be brought into account.

2. About the rate of diazotisation of different substituted amines we meet with but a few investigations.

The first studies go back to the research of HANTZSCH and SCHUMANN[1]). They estimated after different periods the quantity of unchanged nitrite by the reaction of TROMMSDORF (with zinc iodide-amylum solution). As will appear later on, this method is too liable to errors to use it for determining the rates of diazotisation. HANTZSCH operated as follows:

He mixed at 0° 500 c.c. of a solution of the amine ($^1/_{500}$ N. amine hydrochloride + $^1/_{500}$ N. HCl) with 500 c.c. $^1/_{500}$ N. nitrite solution; after 30 minutes he made the first determination. 5 cylinders each with 3 c.c. zinc iodide-amylum solution and 1 c.c. H_2SO_4 were filled

[1]) Ber. **32**, 1691 (1899).

up with water to 100 c.c. Simultaneously he brought in one of the cylinders 1 c.c. of a 0.001 N. nitrite solution and in the other four cylinders different quantities, accurately measured, of the liquid in the reaction vessel. The development of colour was then compared. However the colour does not appear instantaneously and therefore he did not compare the colour till after 15 minutes, though it still increases for some hours.

It is clear, that in analysing each sample the diazotisation is not directly stopped; he allows the colour to develop in acid medium; the diazotisation continues and that with increased intensity because zinc salts are still present, which notably accelerate the diazotisation [1]). Thus considerable errors are made. In this way it was of course impossible to HANTZSCH to examine the course of the diazotisation in the first stages of the reaction. At the same time it should be pointed out that his observations, as he diazotised in a weakly acidified solution will moreover be influenced by the formation of diazo-amino-compounds, which disturbance will vary according to the nature of the amine.

The conclusions drawn by HANTZSCH are as follows:

1st. The rate of diazotisation is extremely great.

2nd. Amines (aniline, p-toluidine, m-xylidine, p-bromaniline, p-nitro-aniline) are diazotised at equal rates (he ascribes differences to inaccuracies in his method) and he concludes from this that the presence of "negative" groups in the amine does not influence the rate of diazotisation.

3rd. The rate of diazotisation is increased by the first excess of acid; however an excess of more than 1 mol. exersises no perceivable influence on the velocity any more.

4th. The diazotisation reaction is bimolecular and answers to the relation:

$$K = \frac{1}{at} \cdot \frac{x}{a-x}.$$

SCHUMANN [2]) has tried to affirm these results in another way. From the fall of electrical conductivity during the diazotisation, occasioned by the consumption of hydrochloric and of nitrous acid, he deduced the rate of the diazo reaction for some amines. In doing this he assumed the substituted aniline-hydrochlorides to have the same affinity constant, and the conductivity of the substituted diazonium salts to be the same [3]). Here some affinity constants follow:

[1]) D.R.P. 171024, 172446, 175593.

[2]) Ber. 33. 527. (1900).

[3]) Ber. 28 1739 (1895).

hydrochlorides of:	temperature	K
aniline	25°	2.44×10^{-5}
p. anisidine	„	8.08×10^{-6}
p. bromaniline	„	1.14×10^{-4}
p. chloraniline	25°	8.56×10^{-5}
m. nitroaniline	„	3.01×10^{-3}
o. „ „	„	2.1
p. „ „	„	9.58×10^{-2}
m. toluidine	„	1.82×10^{-5}
o „	„	3.45×10^{-5}
p. „	„	7.58×10^{-6}

He executed his determinations at 20° and the result was liberation of nitrogen and formation of free HCl:

$$RN_2Cl + H_2O \rightarrow ROH + HCl + N_2.$$

At the same time, as he could only work in a weakly acidified medium, formation of diazo-amino-compounds (especially at 20°) will take place. As SCHUMANN himself states, this amounts to several percentages in the case of *p*-bromaniline. Therefore also this method will not yield reliable results.

After them TASSILLY [1]) occupied himself with the study of the diazotisation reaction. He follows the progress of the diazotisation by determining after different periods the quantity of diazonium salt formed. This diazonium salt namely may be coupled in weakly alcaline medium with SCHÄFFER's salt.

Then he measures the solutions coloured from red to orange with the spectrophotometer of FÉRY in the green-blue part of the spectrum comprised between the marks 180 and 200 of the micrometer, (sodium line at 50) corresponding with $\lambda_1 = 4500$ and $\lambda_2 = 4300$. He sums up his results in the following conclusions:

1. The diazo reaction is bimolecular.

2. Increase of the quantity of acid does not increase the rate of diazotisation of aniline.

3. The diazotisation of sulphanilic acid goes quicker when the concentration both of nitrite and amine is raised.

4. The diazotisation of sulphanilic acid is accelerated by an excess of nitrite.

5. The stability of the diazo solutions may be mutually compared by the help of his method.

We cannot refrain from subjecting his treatise. (Bull. Soc. Chim. Jan. 1920) which gives a review of his researches, to criticism.

[1]) C. R. **157** 1148, **158** 335 en 489.

To begin with, in the first series of his experiments, which are meant to prove that the diazotisation reaction is bimolecular, he uses a nitrite solution containing 0,20 gr. in 1 L., that is a 0.0029 normal solution, whereas theoretically (assuming the nitrite to be 100 %) it should have been 0.0025 normal. This is too high by about 13 %. As even the technically pure nitrite is 96 %, he always works with an excess of the nitrite in respect to the amine. Especially his last determinations will therefore become erroneous.

Casually we may point out that he finds after integration of

$$\frac{dx}{dt} = K(a-x)^2, \quad \text{that} \quad K = \frac{1}{t} \cdot \frac{x}{100-x}$$

while of course this ought to be $K = \frac{1}{100\,t} \cdot \frac{x}{100-x}$. So he finds K a hundred times too great.

Further his determinations do not make the impression of being very accurate. He can read his spectrophotometer only to $^1/_2$ scale division. For the different amines a half scale division however can cause great divergences when we calculate in percentages. As appears from the table below, this may give rise to errors from $1^1/_2$—11 %.

for		aniline	$2^1/_2$ %
,,	*p.*	toluidine	$2^1/_2$ %
,,	*o.*	,,	$1^1/_2$ %
,,	*m.*	xylidine	$2^1/_4$ %
,,	*o.*	anisidine	$2^3/_4$ %
,,	*p.*	,,	$3^1/_2$ %
,,	*p.*	nitraniline	$3^1/_2$ %
,,	*o.*	,,	10 %
,,	*m.*	,,	11 %

The reaction constant of the diazotisation is calculated by Tassilly rather arbitrarily. For instance for p-toluidine he derives it from a determination made after 45 minutes, however it considerably deviates from the K's which we calculated from his determinations relating to other periods. If he had taken the average K, the agreement between the found percentage of inverted amine and the one calculated, would have been much better.

He was more fortunate for p-anisidine. He found 0.142 for K after 30 minutes, while the average of the first four determinations gives $K = 0.143$. (See page 254).

After minutes	Inverted x in %	K as calculated by us	K average	x calculated with $K = 0.060$	x calcul. with $K = 0.0695$
2	18	0.110		10	12.2
15	53	0.076		47	51
30	68	0.071		64	67.5
45	73	0.060	0.0695	73	76
60	82	0.076		78	80.5
75	84	0.070		81	84
90	85	0.064		84	86
300	100	—		94	95.5

Now we have come to a discussion of his results on the influence of an excess of acid on the diazotisation of aniline.

TASSILLY couples 10 c.c. of the diazonium solution, the acidity of which has been mentioned above, with 10 c.c. of the SCHÄFFER's salt solution (containing 3 gr. of SCHÄFFER's salt and 3 gr. of NaOH per liter). As a second experiment he couples 10 c.c. of a diazonium solution containing much more acid, with 10 c.c. of the same solution of SCHÄFFER's salt. Now this diazonium solution contains per liter:

100 c.c. of the amine solution used, makes 0.21 gr. HCl
moreover 100 c.c. 5 % HCl . . . . . 5.— gr. HCl

Total 5.21 gr. HCl

The solution of SCHÄFFER's salt contains 3 gr. NaOH per L., which therefore can neutralise $\frac{3 \times 36.5}{40} = 2.74$ gr. HCl.

So the excess of HCl amounts to 2.47 gr. and consequently the coupling takes place in a solution, containing 1.235 gr. HCl per Liter; the diazotisation therefore can continue and the quantity of inverted amine will be found greater than was in fact diazotised at the moment the sample was drawn. From this we conclude that his experiments in regard to the influences of an excess of HCl on that rate of the diazotisation of aniline cannot be exact.

As to his experiments on the influence of the concentrations of nitrite and amine together, as well as of each apart, on the course of the diazotisation of sulphanilic acid, we must call attention to the fact that TASSILLY tries to diazotise sulphanilic acid with sodium nitrite without the presence of HCl and that without a catalyser. He thinks he studies a quantitative diazotisation in doing this. As we

did not know examples from literature in which diazotisation in this way proceeds quantitatively, we have subjected his experiments to an examination. To this end we worked as follows:

100 cc. $^1/_{100}$ N sulphanilic acid sol. were poured into a beaker, placed in melting ice. As a second liquid, a nitrite sol. was used, containing $^1/_{1000}$ gram-molecule $NaNO_2$ (controlled with $KMnO_4$) per 400 cc. Before the experiment was made both solutions were cooled to 0°; then they were mixed while being well stirred. After 90 minutes (TASSILLY finds 100 % amine inverted after 20 minutes already) we coupled 5 cc. of this solution with 5 cc. of the SCHÄFFER's salt solution as used by him. Then as much strong HCl was poured into the reaction vessel as was necessary to liberate the nitrous acid from the nitrite and to bind the amine. After 20 minutes we again took 5 cc. and coupled them with the same SCHÄFFER's salt solution (5 cc.). After 12 hours the colour was compared with that of experiment n°. 1 in the colorimeter (see next page); the colours were related approximately as 30 : 100. So we may conclude that the diazotisation when HCl is absent, does not become complete. It is evident that because of this, his conclusions sub 3 and 4, based on his researches on sulphanilic acid have no great value.

We see from the preceding that from the researches made till now, nothing can be deduced but that the diazotisation reaction proceeds quickly and is bimolecular. In spite of the imperfections of TASSILLY's research, we thought we could follow his method if only we took care:

1. that the diazotisations were executed under entirely equal circumstances. To this end care was taken that at all times a considerable excess of HCl, in every case the same, was present.

2. that when adding SCHÄFFER's salt, a sufficient quantity of alkali was present in order to stop the diazotisation with certainty.

3. that the determinations were accurately performed.

We attained this by making use of a simple colorimeter according to WOLFF, after having ascertained that the resulting azo dyes complied with BEER's law in the dilutions used by us and that the estimations were not disturbed by the presence of amine not yet inverted. We proceeded as follows:

In a beaker, placed in melting ice 100 c.c. $^1/_{100}$ N. amine hydrochloride were poured, containing at the same time 5 c.c. HCl (spec. gr. 1.19) per Liter, in order to prevent the formation of diazo amide compounds and to set free HNO_2. As the second liquid a nitrite solution was taken, which contained $^1/_{1000}$ gram. mol. NaNO in 400 c.c. (controlled with $KMnO_4$). Before the beginning of the experi-

ment both solutions were cooled to 0°; then they were mixed while being well stirred. So in 0.5 L. are present one millimol of amine, one millimol of $NaNO_2$ and about 6 millimol HCl.

After different periods 5 c.c. samples were drawn with a pipette, which had been cooled to 0° and coupled with 5 c.c. of a SCHÄFFER's salt solution (3 gr. of SCHÄFFER's salt + 3 gr. of NaOH per L.); then an excess of alkali is present, so that the diazo reaction is brought to a stand-still. We executed the coupling reaction at 0° in order to evade every decomposition of diazonium compound.

From determinations performed in the laboratory for Physical Chemistry of the Technical High School here at Delft, we knew, that at 0°, even after 6 hours, we need not fear decomposition of the diazonium-compounds; this disturbance appears only at 20°. Below we cite some affinity-constants for these reactions, in which N_2 is split off:

For	aniline	$K_{30°} = 0.0064$	$K_{35°} = 0.0124$	$K_{40°} = 0.0248$
„	*p.* nitraniline	$K_{35°} = 0.000869$	$K_{40°} = 0.00136$	
„	sulphanilic acid	$K_{46.8°} = 0.0033$	$K_{51.7°} = 0.0078$	$K_{57°} = 0.0108$

From the coloured solutions, thus obtained after coupling, again 5 c.c. were measured and diluted to 500 c.c. (with higher concentrations BEER's law did not hold good). Assuming the last sample taken after about 6 hours to represent 100 %, we compared this standard solution in a colorimeter with the colours obtained from the samples after 2, 4, 6, 10 etc. minutes. In this way we could directly read the percentage of inverted amine.

Finally it should be observed that we used distilled water for all our experiments, as water from the main possessed too much colour of its own.

Below we give same numerical data.

No.	After min.:	% amine inverted.	100 K.	No.	After min.:	% amine inverted.	100 K.
1. Aniline.				2. m. Xylidine.			
1	2	17.4	0.105	1	4	28.8	0.101
2	4	28.9	0.102	2	6	35.2	0.091
3	6	36.0	0.094	3	8	42.0	0.090
4	8	43.4	0.096	4	10	46.8	0.088
5	10	47.5	0.091	5	15	55.7	0.084
6	15	57.2	0.090	6	20	63.0	0.085
7	20	63.8	0.089	7	30	72.5	0.088
8	30	71.9	0.085	8	53	81.5	0.083
9	60	85.9	0.102	9	89	88.1	0.083
10	105	91.3	0.100	10	152	93.4	0.093
11	170	94.8	0.107	11	240	100.0	—
12	260	100.0	—	12	345	100.0	—
13	360	100.0	—				
		Average: 0.0965				Average: 0.0886	
3. o. toluidine.				4. p. toluidine.			
1	$2^1/_6$	18.2	0.102	1	5	26.5	0.072
2	7	42.1	0.104	2	10	38.8	0.063
3	12	52.0	0.090	3	15	51.2	0.070
4	17	60.3	0.089	4	$20^1/_4$	57.1	0.066
5	22	65.9	0.088	5	30	65.0	0.062
6	30	73.6	0.093	6	40	72.5	0.066
7	45	80.6	0.092	7	55	77.9	0.064
8	60	83.3	0.083	8	70	80.9	0.061
9	80	88.0	0.092	9	100	88.7	0.078
10	110	91.3	0.095	10	130	91.7	0.085
11	180	97.5	—	11	190	97.2	—
12	320	100.0	—	12	280	98.5	—
13	360	100.0	—	13	320	100.0	—
				14	360	100.0	—
		Average: 0.0928				Average: 0.0687	

No.	After min.	% amine inverted.	100 K.
	5. m-toluidine.		
1	2	21.2	0.135
2	4	36.0	0.141
3	6	45.9	0.141
4	10	56.8	0.131
5	15	65.9	0.129
6	25	76.5	0.130
7	40	84.9	0.141
8	94	93.2	0.146
9	164	97.0	—
10	258	100.0	—
11	380	100.0	—
		Average:	0.137
	7. p-chloraniline.		
1	1	13.8	0.159
2	2	24.4	0.161
3	4	39.2	0.161
4	7	51.4	0.151
5	11	62.5	0.151
6	15	69.2	0.150
7	25	79.0	0.150
8	45	87.0	0.149
9	60	90.1	0.152
10	90	93.1	0.150
11	211	97.0	0.153
12	271	100.0	—
13	360	100.0	—
		Average:	0.153

No.	After min.	% amine inverted.	100 K.
	6. o-chloraniline.		
1	2	49.6	0.492
2	4	67.9	0.526
3	7	77.0	0.478
4	13	86.0	0.473
5	18	89.0	0.456
6	26	98.5	0.474
7	35	94.4	0.482
8	50	96.8	—
9	65	92.5	—
10	80	100.0	—
11	147	100.0	—
12	360	100.0	—
		Average:	0.483
	8. m-chloraniline.		
1	4	36.3	0.143
2	6	45.5	0.140
3	8	51.6	0.134
4	10	59.5	0.147
5	15	66.6	0.135
6	20	72.5	0.132
7	30	79.6	0.130
8	60	88.0	0.122
9	120	92.4	—
10	210	98.4	—
11	300	100.0	—
12	360	100.0	—
		Average:	0.135

No.	After min.:	% amine inverted.	100 K.	No.	After min.:	% amine inverted.	100 K.
9. o-bromaniline.				10. p. bromaniline.			
1	2	48.2	0.465	1	3	28.1	0.130
2	4	64.2	0.448	2	6	44.3	0.132
3	6	72.8	0.445	3	9	53.6	0.128
4	8	77.9	0.440	4	12	60.4	0.127
5	10	81.8	0.449	5	17	67.7	0.124
6	15	87.0	0.440	6	25	76.1	0.128
7	20	90.1	0.455	7	40	84.0	0.131
8	30	93.2	0.456	8	55	88.3	0.137
9	50	97.1	—	9	121	94.0	0.129
10	105	99.8	—	10	180	95.7	0.124
11	172	100.0	—	11	240	100.0	—
12	380	100.0	—	12	360	100.0	—
		Average: 0.450				Average: 0.129	
11. m. bromaniline.				12. o-iodaniline.			
1	2	21.5	0.137	1	2	47.1	0.445
2	$4^1/_2$	41.0	0.154	2	4	62.8	0.422
3	$6^1/_4$	47.3	0.137	3	7	75.1	0.431
4	9	55.3	0.137	4	12	86.0	0.513
5	12	61.2	0.140	5	17	91.0	—
6	16	68.0	0.133	6	27	95.3	—
7	20	72.2	0.130	7	45	97.9	—
8	32	82.2	0.143	8	85	99.6	—
9	45	86.8	0.146	9	147	100.0	—
10	115	95.0	0.165	10	227	100.0	—
11	180	97.2	—	11	300	100.0	—
12	300	100.0	—	12	360	100.0	—
13	350	100.0	—				
		Average: 0.142				Average: 0.453	

No.	After min.:	% amine inverted.	100 K.	No.	After min.:	% amine inverted.	100 K.
	13. p-iodaniline.				14. m. iodaniline.		
1	2¼	29.3	?	1	2	23.4	0.153
2	4½	42.7	0.165	2	4	37.8	0.152
3	6	49.0	0.160	3	7	50.7	0.147
4	10	58.9	0.143	4	10	59.5	0.147
5	15	69.3	0.150	5	15	70.0	0.155
6	30	81.0	0.142	6	20	76.0	0.158
7	45	86.5	0.142	7	30	81.9	0.151
8	75	91.9	0.151	8	45	87.1	0.150
9	152	98.0	—	9	110	96.9	—
10	255	100.0	—	10	178	98.0	—
11	360	100.0	—	11	265	100.0	—
				12	400	100.0	—
		Average: 0.1505				Average: 0.1515	
	15. Orthanilic acid.				16. Sulfanilic acid.		
1	1	52.1	1.09	1	1	19.4	0.241
2	2	65.1	0.93	2	2	33.0	0.246
3	5	83.6	1.02	3	4	49.5	0.245
4	7	87.6	1.01	4	6	59.6	0.246
5	13	92.0	0.89	5	8	66.5	0.248
6	28	96.3	0.93	6	11	73.1	0.247
7	43	97.2	0.81	7	15	78.9	0.249
8	58	98.1	0.89	8	25	86.1	0.248
9	180	99.5	1.11	9	47	92.2	0.251
10	240	100.0	—	10	120	97.1	0.279
11	300	100.0	—	11	270	100.0	—
12	360	100.0	—	12	320	100.0	—
		Average: 0.966				Average: 0.247	

No.	After min.:	% amine inverted.	100 K.	No.	After min.	% amine inverted.	100 K.
	17. Metanilic acid.				18. Anthranilic acid.		
1	2	17.5	0.106	1	1	63.9	1.77
2	5	33.4	0.100	2	2	77.2	1.70
3	12	58.0	0.115	3	4	86.8	1.64
4	27	75.0	0.111	4	6	91.6	1.81
5	45	82.4	0.104	5	9	93.8	1.68
6	60	86.1	0.103	6	14	96.5	1.97
7	90	90.4	0.105	7	20	98.7	—
8	114	92.6	0.109	8	30	100.0	—
9	187	96.9	—	9	60	100.0	—
10	240	99.1	—	10	120	100.0	—
11	300	100.0	—	11	240	100.0	—
12	360	100.0	—	12	360	100.0	—
		Average: 0.107				Average: 1.761	
	19. p-amidobenzoic acid.				20. m-amidobenzoic acid.		
1	2¼	56.2	0.570	1	4½	39.5	0.145
2	4	67.1	0.510	2	7¼	50.0	0.138
3	7	78.0	0.507	3	14	66.5	0.142
4	10	83.5	0.506	4	23	75.4	0.125
5	15	88.3	0.503	5	38	82.6	0.173
6	22	92.1	0.530	6	63	91.6	—
7	55	97.1	—	7	137	97.1	—
8	122	99.5	—	8	193	100.0	—
9	177	100.0	—	9	255	100.0	—
10	230	100.0	—	10	300	100.0	—
11	300	100.0	—	11	360	100.0	—
12	360	100.0	—				
		Average: 0.521				Average: 0.145	

No.	After minutes:	% amine inverted.	100 K.
	21. m-nitraniline.		
1	1¼	57.0	1.06
2	4½	82.5	1.12
3	6	87.5	1.19
4	8	90.6	1.12
5	10	91.8	1.04
6	15	94.0	1.27
7	20	96.2	(1.41)
8	30	97.7	(1.83)
9	45	98.8	—
10	60	99.4	—
11	95	100.0	—
12	120	100.0	—

Average: 1.13

The following table contains a survey of the average values of the constants, while the graphs 1—6 reproduce some of the series of observations.

Velocity-constants of the diazo reaction: 100 K.

$C_6H_5NH_2 = 0.0965$ $o.p\ (CH_3)_2\ C_6H_3NH_2 = 0.0886$

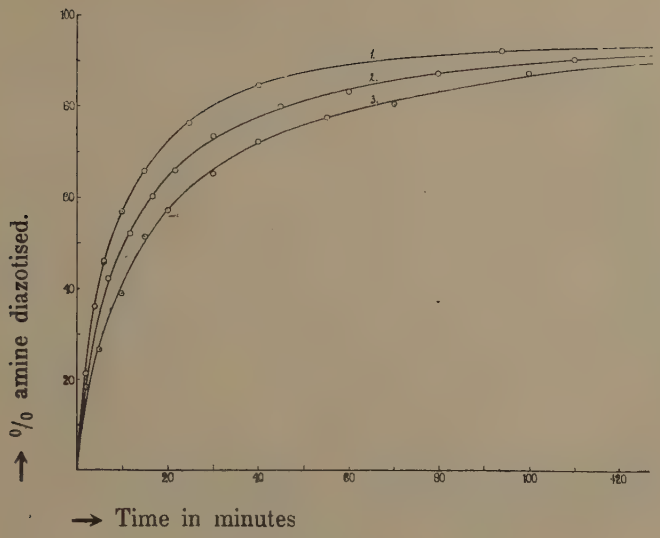
o-$CH_3C_6H_4NH_2$	= 0.0928	*o*-$ClC_6H_4NH_2$	= 0.483	*o*-$BrC_6H_4NH_2$	= 0.450
p- „	= 0.0687	*p*- „	= 0.153	*p*- „	= 0.129
m- „	= 0.137	*m*- „	= 0.135	*m*- „	= 0.142
o-$I_4C_6H_4NH_2$	= 0.453	*o*-$SO_3HC_6H_4NH_2$	= 0.966	*o* $COOHC_6H_4NH_2$	= 1.76
p- „	= 0.151	*p*- „	= 0.247	*p*- „	= 0.521
m- „	= 0.150[5]	*m*- „	= 0.107	*m*- „	= 0.145

From the results of our first series of experiments we have been able to draw the following conclusions:

1. In concordance with the researches cited above, the diazo reaction proved to be bimolecular under the given circumstances.

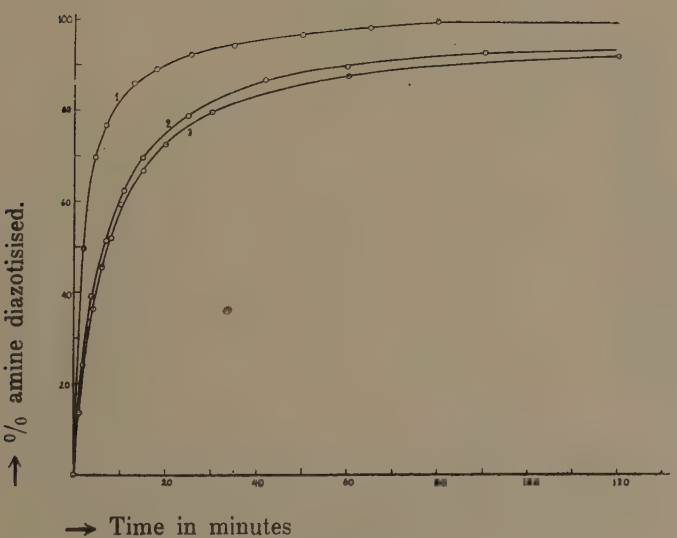
2. When a group has been introduced into aniline, it will especially influence the diazotisation velocity, if it is situated in the ortho-place; in the paraderivative the influence is less strong, in the meta-derivative it is commonly feeble (fig. 1, 2 and 3).

Fig. 1.



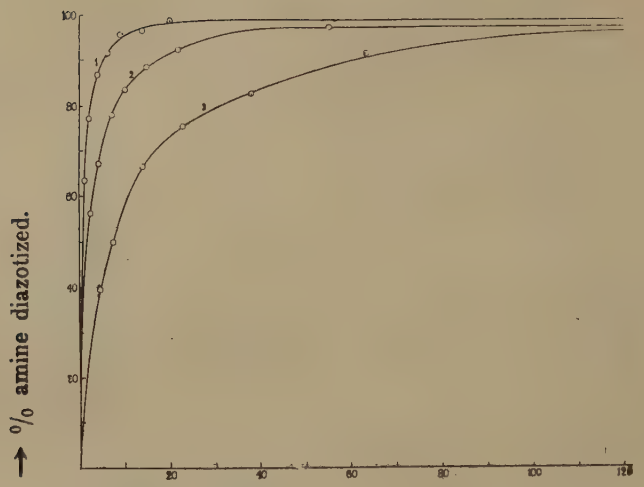
1. *m*-toluidine
2. *o*- „
3. *p*- „

Fig. 2.



1. *o*-chloraniline
2. *p*- „
3. *m*- „

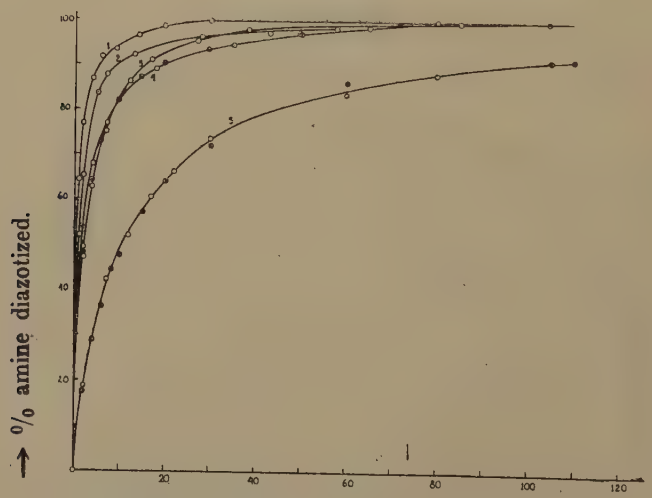
Fig. 3.



1. *o*-amidobenzoic acid
2. *p*- " "
3. *m*- " "

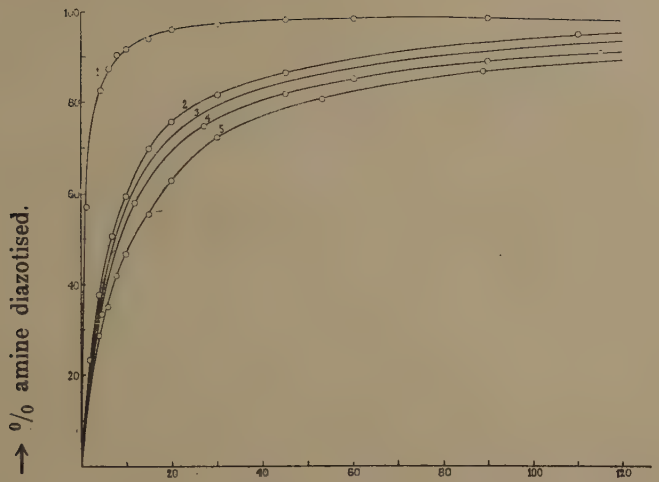
3. As appears from the figures 4, 5 and 6, the velocity of diazotisation increases with the negativeness of the substituent.

Fig. 4.



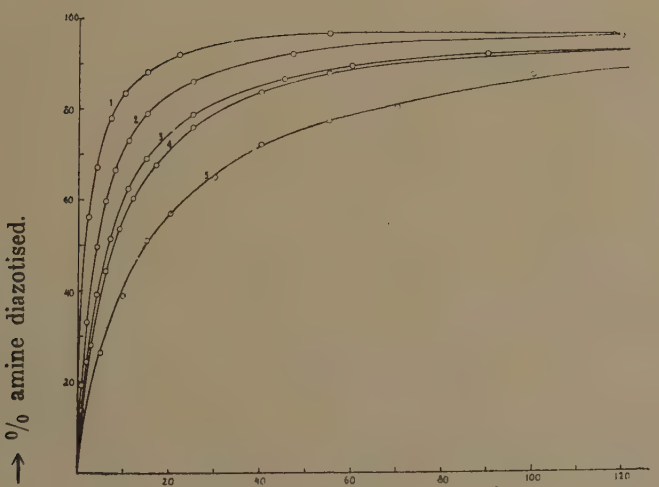
1. anthranilic acid
2. orthanilic acid
3. *o*-iodaniline
⊖ *o*-bromaniline
4. *o*-chloraniline
⊕ aniline
5. *o*-toluidine

Fig. 5.



1. *m*-nitraniline
2. *m*-iodaniline
3. *m*-bromaniline, *m*-chloraniline, *m*-toluidine, *m*-amidobenzoic acid
4. metanilic acid
5. *m*-xylidine

Fig. 6.



1. *p*-amidobenzoic acid
2. sulfanilic acid
3. *p* iodaniline, *p*-chloraniline
4. *p*-bromaniline
5. *p*-toluidine

We hope to collect further information by subsequent series of experiments (which have already been commenced) in which in the first place attention will be paid to the basicity of the amines.

The last communication of TASSILLY (Bull. Soc. Chim. January 1920) led us to the publication of these first results.

Lab. for Organic Chemistry of the Technical High School.

Delft, February 1920.

Physics. — *"On the Critical Quantities of Mercury in Connection with the Increase of the Molecular Attraction on Dissociation of the Double Molecules."* I. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of May 29, 1920).

1. Already twice I published [1]) discussions of the critical quantities of mercury. Starting from the fundamental value $b_c = 150.10^{-5}$ holding for 1 gr. atom Hg (calculated from the densities of the *solid* halogen compounds) and the value $\sqrt{a_c} = 11.10^{-2}$ derived from it (in connection with the critical temperatures of the said compounds), I calculated for mercury, assuming — what is confirmed in different ways — that this substance is quite or almost quite *bi-molecular* at T_c (cf. among others loc. cit. p. 9):

$$T_c = 1260°\text{ abs. } (= 987°\text{ C.}); \quad p_c = 192\text{ atm.}$$

From determinations of the vapour pressure the pressure corresponding to $T = 1260°$ abs. was calculated < 204 atm. (loc. cit. p. 14). When T_c and p are both assumed to be unknown, the same vapour-pressure observations, on assumption of $\sqrt{a_c} = 2 \times 11.10^{-2}$, yield for T_c the value 1242° abs., p_c becoming $= 187$ atm. (loc. cit. p. 15).

In the second of the cited papers I made use of COLARDEAU and RIVIÈRE's later vapour pressure observations (1900), which go up to 880°. With $b_c = 149.10^{-5}$, $\sqrt{a_c} = 10{,}74.10^{-2}$ (for 1 Gr. atom.; likewise determined from these observations), I now calculated (loc. cit. p. 144):

$$T_c = 1172°\text{ abs. } (= 899°\text{ C.}); \quad p_c = 180\text{ atm.,}$$

while for D_c about 3,3 was found. Through a simple calculation I got at the same time the *certainty* that mercury is practically quite bi-molecular at T_c (cf. loc. cit. p. 139—140).

The same value $b_c = 149.10^{-5}$ follows also from the limiting density 14,46 at the absolute zero, when 1,2 is assumed for the (reduced) coefficient of direction of the "theoretical" straight diameter. [I determined before $b_c = 120.10^{-5}$ per Gr. atom. for mercury itself, starting from $D_c = 3{,}77$, calculated by GULDBERG (l. c. p. 8)].

[1]) Cf. among others These Proc. **19**, p. 6 (1916); **20**, p. 138 (1917). Also Zeitschr. für anorg. Chemie **104**, p. 84 and 126 (1918).

2. It appeared, however, more and more that the critical temperature of mercury lies much higher than 900° or 1000° C.

TRAUBE and TEICHNER found no critical phenomena at 1000° C., and HAPPEL [1]) calculated $T_c = 1370°$ abs. ($= 1097°$ C.), $p_c = 456$ atm, from different observations. This would, therefore, be only 100° higher than my first estimation. W. C. MENZIES [2]) came to 1275° C. (675 atm.), while it became clear from KÖNIGSBERGER's experiments [3]) that the long sought critical temperature must lie above 1400° C. (1000 atm.). At ± 1200° C. the meniscus becomes flat; only the liquid is luminous. Below 1400° C. there are seen small glowing drops, which rise from the liquid and fall back into it, or dissolve in the not-luminous vapour. At 1400° C. the emission of light of the liquid rapidly diminishes, and the critical temperature seems to be near.

Then followed Miss J. BENDER's experiments [4]) giving determinations of density of liquid and vapour up to 1400° C. At 1400° C. the vapour was still *quite transparent*; "the distance of the mercury atoms, therefore, is still so great that the electron cannot yet detach itself from the atom, and can, therefore, not yet take charge of the conduction of the electricity." At 1500° C. (one observation) [5]) there was still liquid mercury present.

When the observed densities are represented in a T,v-diagram, we arrive through graphical interpolation at $T_c = 1400°$ C. about, or slightly higher, hence about 1700° abs. (1427° C.), whilst p_c must be at the least 1100 atm. For the critical density about 4,15 is found. (GULDBERG calculated 3,8).

3. It is the question if this high critical temperature of ± 1700° abs. can be theoretically justified. For this purpose it is required, as we shall see, to modify the values of b_c and $1/a_c$ for 1 Gr. atom of mercury somewhat. Instead of $10^5 b_c = 150$ the lower value of about 120 must be assumed for it, while instead of $10^2 1/a_c = 11$ it is necessary to assume 10 (hence $10^4 a_c = 100$ instead of 121).

That at such a high temperature as 1700° abs. the values of a

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[1]) Ann. der Ph. (4) **13** (1904), p. 340 and 620.

[2]) Am. Chem. Soc. **35** (1913), p. 1065.

[3]) Chem. Zg. **36** (1912), p. 1321. Cf. also ROTINJANZ and SUCHODSKI, Ann. Inst. Pol. P. le Grand **23** (1915), p. 668.

[4]) Physik. Zeitschr. **16** (1915), p. 246; **19** (1918), p. 410.

[5]) Neither KÖNIGSBERGER, nor Miss BENDER state clearly in what way their observations of the temperature have been made. This remains in my opinion the weak point.

and b will be *smaller* than those which have been determined at the critical temperatures of the mercury-halogenides (which temperatures lie in the neighbourhood of 1000° abs.) is, indeed, to be expected. For it is known that b and a decrease with increasing temperature.

But there is still something else required. If such a high critical temperature and pressure is to be reached, the double molecules must be dissociated at T_c to a slight amount. As at this dissociation the value of a is greatly increased ($10°\sqrt{a_c}$ becomes 40 per Gram-atom of the isolated atoms as against 10 in the double molecules), the calculation (which we shall give in the second part of this paper) shows that, even in case of a slight degree of this dissociation, in the formula a pretty large factor will appear for T_c on account of the large value of da/dx, which will increase the value of T_c by about 30 %, and can consequently raise the value of p_c to *more than four times* the amount of the original value (Cf. also § 8).

Hence it is not because in consequence of this slight degree of dissociation x the value of a_c itself is appreciably increased, and consequently T_c and p_c (which are both proportional to a_c) are likewise increased in the same degree (for this the increase of a_c at so slight a degree of dissociation is much too small) — but because in consequence of this dissociation, *in connection with the very high value of* da/dx, the formula which expresses T_c in a_c obtains a *factor* that is a function of x and da/dx, and through which T_c is increased by the said amount of e.g. 30 %, even though the dissociation of the double molecules is only slight. And *in consequence* of this factor in T_c the formula for

$$p_c = \frac{RT_c}{v_c - b_c} - \frac{a_c}{b_c}$$

will undergo such a modification that p_c is not increased by 30 %, but by more than 300 %.

Thus the extraordinary circumstances connected with the critical temperature and pressure of mercury have induced me to extend my former theory concerning the critical quantities on association [1]) for the special very important case that a is considerably increased

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[1]) Arch. Teyler (2) **11**, 3e Partie (1908), p. 1—96; These Proc. **17** (1914), p. 598 We remind the reader that *the mere fact of the dissociation at* T_c (hence $\triangle b$ and $\triangle a = 0$) causes the values of T_c and p_c to increase considerably. Thus we found for $x = 1/3$ already an increase of 10,6% for T_c; for $x = 1/2$ of 11,5 %, and for $x = 2/3$ of 9,9 % (for $x = 0$ and $x = 1$ the factor is of course $= 1$), i.e. for ideal substances. For "ordinary" substances and for the cases that in the association e.g. $\triangle b$ is not $= 0$, these amounts are considerably increased. And as regards p_c, these

in consequence of the dissociation of the double molecules. According to my recent investigations, this case is met with everywhere where the dissociation (as for Hg_2) leads to *free atoms*, for which the increased attractions of valency are so enormously much greater than for the compounds [1]).

4. Vapour Pressures and Values of the Vapour Densities D_2.

We shall start with the treatment of the experimental material known at present. To supplement this, it is however necessary approximately to know the values of D_2 (the density of the saturate vapour). But for this purpose first the values of the vapour pressures must be known in approximation.

When the critical temperature is assumed $=$ 1427° C. $=$ 1700° abs., and $p_c = 1100$ atm., then follows from the known formula

$$log \frac{p_c}{p} = f\left(\frac{T}{T} - 1\right)$$

at 100°, 200°, 300°, 500°, 700° and 880° C., where p resp. $= 0{,}28$ mm., 17,2 mm., 246 mm., 8 atm., 50 atm. and 162 atm. [2]):

$$f_{10} = 1{,}82 \quad 1{,}81 \quad 1{,}80 \quad 1{,}78 \quad 1{,}80 \quad 1{,}75.$$

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increases become resp. 47,7, 54,3 and 47,6 % for ideal substances with the same values of x. Hence already on an average 50 % between $x = 1/3$ and $x = 2/3$, which amount is still *considerably increased* for ordinary substances, and for the case that $\angle b$ is not $= 0$.

But when besides $\angle a$ is so enormously large as in mercury e.g. (formerly we always supposed $\triangle a = 0$, because we had only to do with substances that do not appear as isolated atoms with the so greatly increased attractions of valency), T_c and especially p_c is increased in a still *much greater degree*, even though the value of x be only slight.

[1]) These Proc. 18—21; especially 21 (1918), p. 644. Cf. also Z. f. anorg. Ch. 104, 56—156 (1918) and J. d. Ch. Ph. 16 (1918), p. 411.

[2]) $p_c = 1150$ atm. instead of 1100 atm. would give 1,83 for the first value of f, 1,80 for the last, which would render the almost constant course of this quantity still slightly better. The more p_c is assumed to be below 1100 atm., the greater the unjustifiable decrease of the f-values on rise of the temperature. The value of 1100 atm. is therefore to be regarded as a minimum, and p_c will sooner be found somewhat greater than this amount than smaller. We remind that the course of the values of f is a strict criterion for the determination of the critical pressure. For in the neighbourhood of the critical temperature these values always increase on rise of temperature; for ordinary substances there is a minimum at about $T = 3/4\ T_c$; for substances as *He*, H_2, etc., where a continually decreases instead of increasing at falling temperature, f will also continue to decrease from T_c to lower temperatures, without passing through a minimum. (Cf. also Recueil des Tr. Ch., Nº. 3 and 5 of 1920).

With $f_{10} = 1{,}8$ $(f = 4{,}14)$ [1]) and $p_c = 1100$ atm. the following values are further calculated for the temperatures above 880° C.

	900°	1000°	1100°	1200°	1300°	1400°	1427° C.
$p =$	171	274	410	581	787	1029	1100 atm.

We can now easily calculate the values of D'_2 from the subjoined values of the vapour pressures, on the supposition that the vapour is and remains monatomic, and besides continues to follow the laws of the ideal gases.

t	p	D_2' (calc.) (ideal)	D_2 (found)	$\frac{D_2 \text{ (found)}}{D_2' \text{ (ideal)}}$
100° C.	0,28 mm.	0,0000	—	—
200°	17,2 „	0,0001	—	—
250°	74,1 „	0,0005	—	—
300°	246 „	0,0014	—	—
350°	670 „	0,0034	—	—
400°	2,06 atm.	0,0076	—	—
500°	8,0 „	0,0253	—	—
600°	22,3 „	0,0624	—	—
700°	50 „	0,126	—	—
800°	102 „	0,232	—	—
900°	171 „	0,356	—	—
1000°	274 „	0,526	0,55	1,05
1100°	410 „	0,730	0,80	1,10
1200°	581 „	0,964	1,15	1,19
1300°	787 „	1,222	1,65	1,35
1400°	1029 „	1,503	2,60	1,73
$T_c = 1427°$	$1100 = p_c$	1,581	$(4{,}15) = D_c$	2,62

The "found" values of D_2 have been graphically interpolated from the following values of D_2, determined by Miss BENDER.

	1050°	1210°	1230°	1295°	1330°	1380° C.
$D_2 =$	0,70	1,15	1,35	1,65	1,90	2,50

[1]) It appears from this value of f that — at least at temperatures below 1000° C. — mercury behaves almost as an ideal substance (for them $f_c = 4$, and $f < 4$ below T_c).

The "calculated" values of D_2 have been determined from $v_2 = RT : p$ for 1 Gr. atom, hence $v_2 = \frac{RT}{p \times M} \times 22415$ cm³ for 1 Gr., when p is given in atm. and $R = 1 : 273.1$. Hence we have:

$$D'_2 = \frac{p}{T} \times \frac{200{,}64}{22415 : 273{,}1} = \frac{p}{T} \times \frac{200{,}64}{82{,}08} = \frac{p}{T} \times 2{,}444.$$

It appears from the value at 1000° that at this temperature the vapour is still mon-atomic, and the deviation from the law of BOYLE is still very slight. The deviation increases more and more, and close to the critical temperature the vapour will be almost bi-molecular like the liquid. As D (calc.) : D (found) is about 2,6 at T_c, the deviation from the law of MARIOTTE would be there about 2,6 : 2 = 1,3. In an ideal substance $s = 2{,}67$; in an ordinary substance $s = 3{,}8$ to 4. We see therefore, that the normal value of s is very considerably decreased in consequence of the greatly increased value of p_c through the small dissociation of the double molecules at T_c. Also the values of v_c and T_c are modified by this, but not in the same degree as p_c. The result is accordiugly that, whereas p_c is more than four times greater than the normal value in case of non-dissociation of the double molecules, s will be about 3 times smaller than the normal value 3,8 to 4, i.e. 1,3.

We shall discuss this more at length in § 8.

5. The values of D_1 and $D_1 + D_2$.

We now proceed to the values of D_1, i.e. those of the liquid densities. At the same temperatures (to which three more temperatures below 100° C. have been added) the following values are found. The "found" values of $D_1 + D_2$ (see table following page) have been obtained by addition of the above found values of D_2 to those of D_1.

The "found" liquid densities D_1 above 350° C. are graphically interpolated from the following values determined by Miss BENDER.

	500°	600°	800°	900°	1000°	1100°	1130°	1200°	1270°	1320° C.
$D_1 =$	12,5	12,15	11,6	11,15	10,55	10,0	9,40	8,85	8,25	7,8

As regards the "calculated" values of $D_1 + D_2$, they were calculated from 0° to 350° from

$$D_1 + D_2 = 13{,}5956 - 0{,}0024507\, t + 0{,}0_6 2089\, t^2, \quad . \quad . \quad . \quad (a)$$

in which the coefficients of t and t^2 were calculated from the observations at 150° and 300° C. The calculated and the found

t	D_1 (found)	D_2 (found)	$D_1 + D_2$ (found)	$D_1 + D_2$ (calc.)
(trip.) — 38°,85 C.	13,6902	—	13,6902	13,6911
0°	13,5956	—	13,5956	13,5956
50°	13,4733	—	13,4733	13,4736
100°	13,3524	—	13,3524	13,3526
150°	13,2327	—	13,2327	13,2327
200°	13,1139	(0,0001)	13,1140	13,1138
250°	12,9957	(0,0005)	12,9962	12,9960
300°	12,8778	(0,0014)	12,8792	12,8792
350°	12,7640	(0,0034)	12,7674	12,7635
400°	12,65	(0,008)	12,66	12,66
500°	12,425	(0,025)	12,45	12,45
600°	12,18	(0,06)	12,24	12,24
700°	11,90	(0,13)	12,03	12,03
800°	11,60	(0,23)	11,83	11,80
900°	11,15	(0,36)	11,51	11,48
1000°	10,55	0,55	11,10	11,12
1100°	9,90	0,80	10,70	10,69
1200°	9,00	1,15	10,15	10,15
1300°	7,80	1,65	9,45	9,46
1400°	6,00	2,60	8,60	8,58
1427°	$(4,15) = D_c$	$(4,15) = D_c$	(8,30)	8,30

values are in good concordance with each other; at 350° a small deviation begins to appear. At — 38°,85 the deviation is still exceedingly slight. The fictitious value D_0 at the absolute zero ($t = -273°,1$ is found $= 14,2804 = 14,28$ (if the mercury were still liquid then).

For temperatures above 350° C. another term must be added to the above formula. As this formula yields somewhat too small values from 400° to about 835°, and on the other hand to an ever increasing degree too large values above 835°, the term

$$16,4.10^{-6}\left(\frac{t}{100}\right)^4\left[8,35 - \frac{t}{100}\right]^{2/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

has been added to (a) from 400°. [1]) The calculation teaches that the deviations from the found values are least, when the exponent of the first factor (viz. $t:100$) amounts to 4, and that of the second factor to $^2/_3$. Every modification in one of the exponents immediately gives not only greater, but *much* greater deviations. [2]) Here follows a survey of the values of the two parts (a) and (b), from 400° C.

	(a)	(b)		
400° C.	12,6486	+ 0,0112	= 12,6598	= 12,66
500°	12,4225	+ 0,0230	= 12,4455	= 12,45
600°	12,2004	+ 0,0376	= 12,2380	= 12,24
700°	11,9825	+ 0,0490	= 12,0305	= 12,03
800°	11,7687	+ 0,0334	= 11,8021	= 11,80
900°	11,5592	− 0,0807	= 11,4785	= 11,48
1000°	11,3538	− 0,2290	= 11,1248	= 11,12
1100°	11,1526	− 0,4598	= 10,6928	= 10,69
1200°	10,9557	− 0,8063	= 10,1494	= 10,15
1300°	10,7627	− 1,3050	= 9,4577	= 9,46
1400°	10,5740	− 1,9985	= 8,5755	= 8,58
1427°	10,5238	− 2,2254	= 8,2984	= 8,30

The first table shows clearly that the thus calculated values are in perfect concordance with the found values. As we have calculated the coefficient $16{,}4.10^{-6}$ of the correction term (b) exclusively from observations up to 1300° (inclusive), the agreement at 1400° C. is the more valuable. We may, therefore, safely assume the calculated value $8{,}30 : 2 = 4{,}15$ to be accurate for the critical density.

6. The Value of D_1—D_2 near T_c and that of γ at different Temperatures.

We have another means to control the approximate correctness of the values of D_1 and D_2 e.g. above 900°, and of that of the

[1]) Below 400° the correction term (b) is no longer valid. For 300° it would yield + 0,0041; for 200° + 0,0009 and for 100° + 0,00006, which values are too great.

[2]) We point out that the exponent $^2/_3$ is assumed not to influence the sign of $8{,}35 - t/_{100}$, so that this remains negative for $t > 835°$.

assumed critical temperature (1427° C.), viz. in the empirical law that below T_c (not *immediately* below T_c, however, where $D - D_2 \therefore \sqrt{1-m}$), the equation

$$D_1 - D_2 = C\sqrt[3]{1-m}$$

holds in approximation, so that $(D_1 - D_2)^3$ is proportional to $1-m$, i.e. to $T_c - T$ ($m = T : T_c$). Now we get the following table

	1000°	1100°	1200°	1300°	1400°
$D_1 - D_2 =$	10,0	9,1	7,85	6,15	(3,40)
$(D_1 - D_2)^3 =$	1000	754	484	233	(39)

so that the four first values of $(D_1 - D_2)^3$ are roughly to each other as 4 : 3 : 2 : 1, which would give the value 1400° C. for T_c.

The corresponding values of $(D_1 - D_2)^3$ are to each other as 100 : 83 : 62 : 38 (: 11,6), i.e. as 5 : 4 : 3 : 2 about, which would point to $T_c = 1500°$ C. And as (except close to T_c) the $\sqrt[3]{}$-law is sooner fulfilled than the $\sqrt[2]{}$-law, T_c will lie nearer to 1400° than to 1500° — in concordance, therefore, with our assumption (1427°). A critical temperature higher than 1500°, as would follow from a few values recorded by Miss BENDER, is in my opinion in conflict with her own observations concerning D_1 and D_2. When the two last values of $(D_1 - D_2)^3$, viz. 38 and 11,6 are taken as criterion of the $\sqrt[2]{}$-law, holding theoretically near T_c, then the value of about 1440° C. would follow from this for T_c.

Let us now examine the (reduced) coefficient of direction of the so-called straight diameter. For the total course between the absolute zero and the critical temperature evidently $2(1-\gamma) = 14{,}28 : 4{,}15 = 3{,}44$ is found, hence $1 + \gamma = 1{,}72$, $\gamma = 0{,}72$. But this amount can only be assigned to the last piece between 1000° C. and T_c, where – in consequence of the increasing association in the vapour-phase — the straight diameter after its almost linear course between — 40° and + 1000° C. suddenly begins to show an appreciable curvature towards the side of the large volumes.

As regards the said part below 1000° (where the vapour phase is still absolutely without influence), we find there e.g. between 0° and 300° C.:

$$2\gamma = \frac{13{,}5956 - 12{,}8792}{300} \times \frac{1700}{4{,}15} = 0{,}9782,$$

hence $\gamma = 0{,}489 = 0{,}49$.

And between 0° and 1000° C.:

$$2\gamma = \frac{13{,}5956 - 11{,}1248}{1000} \times \frac{1700}{4{,}15} = 1{,}012,$$

hence $\gamma = 0{,}506 = \underline{0{,}51}$, almost equal to the value between 0° and 300° C. The value $\gamma = \underline{0{,}5}$ is that which is due to "ideal" substances with a and b invariable (chiefly b no function of v). We saw above that below 1000° C. also the value of f (viz. 4,1) points to the quasi-ideal behaviour of mercury at those comparatively lower temperatures.

7. General Formulae for v_c, T_c, p_c and s.

When v_c is the critical volume (expressed in normal units) of 1 Gr. atom, then

$$D_c = \frac{200{,}64}{22415\, v_c},$$

hence with $D_c = 4{,}15$:

$$v_c = rb_c = \frac{200{,}64}{22415 \times 4{,}15} = \underline{0{,}002157} \quad . \quad . \quad . \quad . \quad (1)$$

Accordingly the value of b_c with given D_c will only depend on r. If e.g. $r = 2$, then b_c would be $= 108.10^{-5}$, but if r should be $= 1{,}8$, b_c would become $= 120.10^{-5}$.

For T_c holds the relation $RT_c = \frac{8}{27}\frac{a'_c}{b'_c} \times \theta$, hence

$$\underline{RT_c = \frac{8}{27} n \frac{a_c}{b_c} \times \theta,} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which a_c and b_c refer to 1 Gr. atom (200,6 Gr. mercury), so that in reality $a'_c = n^2 a_c$ and $b'_c = nb_c$, when $n = 2 : (1 + x)$ represents the factor of association [1]).

In normal cases ($n = 1$ or 2) θ is a factor somewhat smaller than unity, which we before represented by λ. (If e.g. $r = 2$, we find for λ the value $^{27}/_{28}$, whilst for ideal substances ($r = 3$) λ becomes $= 1$).

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[1]) From 1 single molecule (or atom) $= {}^1/_2$ double molecule ${}^1/_2 (1-x) + {}^1/_2 (2x) = {}^1/_2 (1 + x)$ molecules arise on dissociation of the double molecule. These molecules occupy the molecular volume b_c (leaving contraction out of account; this has been reckoned with in the factor θ), so that every molecule on an average occupies the volume $b'_c = b_c : {}^1/_2 (1 + x) = b_c \times 2 : (1 + x)$. If the degree of dissociation x of the double molecules $= 0$, then $n = 2 : (1 + x) = 2$, hence $b'_c = 2b_c$ (all the molecules are then double molecules). And when $x = 1$ (all the molecules single), then $n = 1$ and $b'_c = b_c$. And the same thing holds with regard to $\sqrt{a}$ and v.

But in all cases of association ($n > 1 < 2$) θ will be a function of x, and besides of the contractions Δb and $\Delta\sqrt{a}$, if they exist. As we stated above, this factor can become pretty large, e.g. 1,3.

From $p_c = \frac{RT_c}{v'_c - b'_c} - \frac{a'_c}{v'^2_c}$ after substitution of the above-mentioned value of RT_c, and of $v'_c = nv_c$, $b'_c = nb_c$, $a'_c = n^2 a_c$, we find for p_c:

$$p_c = \frac{1}{27}\frac{a_c}{b_c^2}\left[\frac{8\theta}{r-1} - \frac{27}{r^2}\right] = \frac{1}{27}\frac{a_c}{b_c^2} \times \pi, \quad \ldots \quad (3)$$

when besides rb_c is substituted for v_c. Then with $r = 2$ the factor π becomes therefore $= \frac{8 \times {}^{27}/_{28}}{1} - \frac{27}{4} = 27 \times \left(\frac{2}{7} - \frac{1}{4}\right) = \frac{27}{28}$, just as θ, the factor of RT_c — i.e. in the normal cases ($n = 1$ and 2). And if then $r = 3$, in which $\theta = 1$, then π becomes also $= \frac{8}{2} - \frac{27}{9} = 1$.

But for $n > 1 < 2$ π will again be a function of x, Δb and $\Delta\sqrt{a}$, and in general much greater than θ. If e.g. $\theta = 1{,}363$ (see § 8), $r = 2$, then π becomes $= 10{,}91 - 6{,}75 = 4{,}16$, so that π is more than three times as great as θ. The critical pressure will then be $4{,}16 \times \frac{28}{27} = 4{,}3$ times greater than the normal value for $r = 2$, when there is no association, in which case $\pi = \theta = \lambda = {}^{27}/_{28}$ [1]).

From (1), (2) and (3) the following equation follows now further with $v'_c = nv_c = n \times rb_c$:

$$s' = \frac{RT_c}{p_c v'_c} = \frac{8}{r} \times \frac{\theta}{\pi}, \quad \ldots \quad (4)$$

in which $s' = s : n$ (where s refers, therefore, to v_c per Gr. atom). Now we do not find $rs' = 8$ as in normal cases — but

$$rs' = 8 \times \frac{\theta}{\pi}, \quad \ldots \quad (4a)$$

in which $\theta : \pi$ can be ${}^1/_3$ in some cases (see above). In consequence of this s' may be reduced from 4 (the normal value for $r = 2$) to $4 : 3 = 1{,}3$, i.e. to the *third* of this normal value. (See the table in

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[1]) We found before that in normal cases $\theta = \pi$. Then $\theta = \frac{8\theta}{r-1} - \frac{27}{r^2}$, from which $\lambda = \theta = \frac{{}^{27}/_{r^2}}{8 : (r-1) - 1}$. When in this $(1+\gamma) : \gamma$ is substituted for r, in which γ represents the reduced coefficient of direction of the straight line between D_c and ${}^1/_2 D_0$ in a D,T-diagram, we find back $\lambda = \frac{27}{8\gamma - 1}\left(\frac{\gamma}{\gamma+1}\right)^2$, the formula derived by me, yielding $\lambda = 1$ for $r = 3$ ($\gamma = 0{,}5$) and $\lambda = {}^{27}/_{28}$ for $r = 2$ ($\gamma = 1$).

§ 4, in which we found for D_c (found) : D_c (MARIOTTE) the value $2{,}62 : 2 = 1{,}31$, when n is practically $= 2$ at T_c. The great decrease of s' is, therefore, almost exclusively owing to the exceedingly great increase of p_c with comparatively little changed value of T_c and of v_c. (the latter in consequence of a slight modification in the value of r).

8. Calculation of θ and π, and of a_c and b_c from the given Values of T_c, p_c and v_c.

If $T_c = 1700$ (abs.), $p_c = 1100$ (atm.), and $v_c = 215{,}7 \cdot 10^{-5}$ according to (1), we find for $s' = s : n$ the value (cf. also the table in § 4; on the supposition, therefore, that n at T_c is not far from 2):

$$s' = \frac{1700 : 273{,}1}{1100 \times 215{,}7.10^{-5}} : 2 = 1{,}312 \quad . \quad . \quad . \quad . \quad . \quad (a)$$

From (4ª) follows for θ, the coefficient of RT_c, from

$$rs' = \frac{8\theta}{\frac{8\theta}{r-1} - \frac{27}{r^2}}$$

the value

$$\theta = \frac{27}{8r^2\left(\frac{1}{r-1} - \frac{1}{rs'}\right)} = \frac{27\,s'}{8r\left(\frac{rs'}{r-1} - 1\right)} \quad . \quad . \quad . \quad . \quad (b)$$

With $s' = 1{,}312$ we find from this the following values for different values of r.

$r =$	2	1,9	1,8	1,7	1,6	1,5
$\theta =$	1,363	1,317	1,260	1,191	1,108	1,005

The factor θ becomes, therefore, smaller as r is assumed smaller, which also follows immediately from the formula (b), if only $r < 3{,}05$, which is of course always the case. It also appears from (b) that θ becomes smaller, if n should be < 2, for then $s' = s : n$ becomes greater.

Then is found for the factor π at p_c:

$$\pi = \frac{8\theta}{rs'} = \frac{27}{r^2\left(\frac{rs'}{r-1} - 1\right)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

yielding

$r =$	2	1,9	1,8	1,7	1,6	1,5
$\pi =$	4,156	4,226	4,268	4,274	4,222	4,087

Hence the factor π increases with decreasing r, as long as r remains $> 1{,}74$ ($\pi = 4{,}277$). For smaller values of r π decreases again.

As $\theta = 1{,}36$ is rather great, $r = v_c : b_c$ will probably lie in the neighbourhood of 1,8 or 1,7 for mercury at the critical temperature [as we shall see from the theoretical concluding part of this paper, this decrease is also a consequence of the degree of dissociation, however small, of the double molecules at T_c, as soon as Δa is great]. Then θ is 1,2 or 1,25 and π in the neighbourhood of its maximum value 4,28.

Let us now examine the values of a_c and b_c, corresponding to the assumed critical data $T_c = 1700°$ abs., $p_c = 1100$ atm., $v_c = 215{,}7 . 10^{-5}$) for different values of r.

From $RT_c v_c = \frac{8}{27} n r a_c \times \theta$ follows $a_c = \frac{27}{8} RT_c v_c : n r \theta = \frac{27}{8} \times \times 134{,}3 . 10^{-4} : n r \theta$, so that $10^4 a_c = 226{,}6 : r\theta$, when $n = 2$.

With regard to b_c we have simply $b_c = v_c : r$; hence $10^5 b_c = 215{,}7 : r$.

This gives the following values of a_c and b_c.

$r =$	2	1,9	1,8	1,7	1,6	1,5
$10^5 b_c =$	107,9	113,5	119,8	126,9	134,8	143,8
$10^4 a_c =$	83,13	90,57	99,91	111,9	127,8	150,3
$10^2 \sqrt{a_c} =$	9,12	9,52	10,00	10,58	11,30	12,26

We see from this that with $r = 1{,}8$— in harmony with the slight degree of dissociation corresponding to the increased critical pressure and temperature — the values $10^5 b_c = 120$, $10^4 a_c = 100$ (per Gr.atom) are about corresponding. $\sqrt{a}$ is then somewhat smaller than the value determined from the mercury halogenides at about 1000° C., viz. $10 . 10^{-2}$ instead of $11 . 10^{-2}$.

By the aid of these values of a_c and b_c we shall now calculate back the values of T_c and p_c by way of check on *two* suppositions.

In the *first place* that mercury were *not* dissociated at the critical temperature, i.e. consisted merely of double molecules ($x = 0$, $n = 2$). If we then suppose that $r = 2$, we should get in this case $v_c = rb_c = 2 \times \times 119{,}8 . 10^{-5} = 239{,}6 . 10^{-5}$ (per Gr.-atom). Further $RT_c = \frac{8}{27} \times 2 \times \times \frac{99{,}91 . 10^{-4}}{119{,}8 . 10^{-5}} \times \frac{27}{28}$, as $\theta = \lambda = 27/28$ corresponds to $r = 2$ (see above); hence $RT_c = 4{,}766$, $T_c = 1302°$ abs. The following equation is then found for p_c:

$$p_c = \frac{1}{27} \times \frac{99{,}91 \,.\, 10^{-4}}{143{,}5 \,.\, 10^{-8}} \times \frac{27}{28} = 248{,}6 = \underline{249 \text{ atm.}}$$

With the now assumed values of a_c and b_c these would be the values of the critical temperature and pressure of perfectly undissociated Hg, at the critical point. They would give for $s' = RT_c : p_c v'_c$ with $v'_c = 2 v_c$ the value $s' = \frac{4{,}766}{248{,}6 \times 479{,}2 \,.\, 10^{-5}} = \underline{4{,}00,}$ which value properly corresponds to $r = 2$.

The equation of state is, of course, also identically satisfied. For $\frac{a_c}{v_c^2}$ is calculated $\frac{99{,}91 \,.\, 10^{-4}}{574{,}1 \,.\, 10^{-8}} = 1740$ atm., so that $v'_c - b'_c = RT_c : (p_c + a_c/v_c^2)$ becomes:

$$2\,(239{,}6 - 119{,}8)\,10^{-5} = \frac{4{,}766}{248{,}6 + 1740{,}3},$$

i.e. $$239{,}6 \,.\, 10^{-5} = 239{,}6 \,.\, 10^{-5}.$$

We may state here that a_c/v_c^2 is also properly $= (f_c - 1)\, p_c = 7 p_c$, because $f_c = 8$ corresponds to $r = 2$.

But all these values are totally changed, when only, in the *second* place, the slightest dissociation of the double molecules exists at T_c, (which we shall further develop theoretically in the second part of this paper).

Let us suppose for convenience that then n remains $= 2$ (x will possibly be 0,01, so that strictly speaking $n = 2 : (1 + x)$ would become 1,98, but in the calculation of θ and π above we have also left $n = 2$), and further that in this case in consequence of the slight dissociation at T_c the value of r would have become 1,8 instead of 2 (this too will be further elucidated in the second part); then v_c becomes $= 1{,}8 \times 119{,}8^3 \,.\, 10^{-5} = \underline{215{,}7 \,.\, 10^{-5}}$. Further with $\theta = 1{,}260$ and $\pi = 4{,}268$ (see above) $RT = 6{,}228$, $\underline{T = 1700 \text{ abs.}}$, $\underline{p_c = 1100 \text{ atm.}}$, all of them being the values from which we have started for the calculation of the factors θ and π, and which will give back the value 1,312 for $s' = \frac{6{,}228}{1100 \times 431{,}4 \,.\, 10^{-5}}$.

Accordingly the value of T_c has become $\frac{28}{27} \times 1{,}26 = \underline{1{,}31}$-times greater, that of p_c $\frac{28}{27} \times 4{,}268 = \underline{4{,}43}$-times greater, and that of s' $\underline{3{,}05}$-times smaller.

The equation of state becomes in this case:

$$2\,(215{,}7-119{,}8)\,10^{-5}=\frac{6{,}228}{1100+2147},\text{ or }192.10^{-5}=192.10^{-5}.$$

Now a_c/v_c^2 is no longer $= 7\,p_c$, but only slightly less than $2p_c$.

In the above discussion we have always supposed n in the neighbourhood of 2. It might, however, be asked, how high e.g. T_c might become, if n was in the neighbourhood of 1. As $\sqrt{a_c}$ would then be $=40.10^{-2}$ (increased attraction of the isolated atoms) instead of 11 à $10\,.\,10^{-2}$, we should get (b remaining $=120\,.\,10^{-5}$):

$$T_c=273{,}1\times\frac{8}{27}\lambda\frac{1600.10^{-4}}{120.10^{-6}}=80{,}92\,\lambda\times 133{,}3=\text{ about }10000^\circ\text{ abs.},$$

whereas in reality T_c will certainly not be far from 1700° abs. Total dissociation of Hg_2 into $Hg + Hg$ is, therefore, impossible at the critical point. Only a value of x in the neighbourhood of 0 (n in that of 2) can represent the critical quantities as determined experimentally.

In this first paper we have only specified the experimental data known at present more closely, and drawn from them all the consequences to which these data gave occasion. *If* really $v=216\,.\,10^{-5}$, $T_c=1700°$ abs. and $p_c=1100$ atm. — and there is no longer any doubt that this will appear to be the case approximately — *then* belong to the values of r mentioned in § 8 the values of θ and π placed under them, viz. the factors for RT_c and p_c in consequence of the small degree of association at T_c in connection with the very great value of $\Delta\sqrt{a}$. And this on the strength of the relations derived in § 7, which are of general validity.

But this is only the foundation of our real task. *To supplement our former theory of the critical quantities on association,* we must now examine *theoretically* what follows, in the case of such great values of $\Delta\sqrt{a}$ on dissociation, from $\frac{dp}{dv}=0$ and $\frac{d^2p}{dv^2}=0$, and derive the relations which are valid for $r=v_c:b$, and also for θ, the factor of T_c — all in function of the degree of dissociation x and of $\Delta\sqrt{a}$. Then the value of π, the factor of p_c, is known at the same time.

And then we shall also be able, on account of the found formulae for r and θ, to define more closely the values of them; which was not yet entirely possible in this paper, because the choice between different values of r had still remained open.

La Tour près Vevey, spring 1920. *To be continued.*

I state with pleasure that the execution also of this work has been greatly facilitated by the aid of the VAN 'T HOFF-fund, for which I express my thanks to the board.

Physics. — *"On the Critical Quantities in the Case of Association, when the Molecular Attraction is considerably Increased on Dissociation of the Molecules to the Isolated Atoms, also in Connection with the Critical Quantities of Mercury"*. II. (Conclusion). By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of June 26, 1920).

§ 9. General Relation for the Degree of Dissociation x of the Double Molecules.

If Z is the thermodynamic potential of the mixture of double and single molecules, then it may assumed to be known that[1])

$$Z = n_1 C_1 + n_2 C_2 - \int p\, dv + pv + RT\,(n_1 \log n_1 + n_2 \log n_2),$$

when n_1 and n_2 represent the number of molecules resp. of the single and the double molecules, and C_1 and C_2 are given by

$$\left.\begin{aligned} C_1 &= -k_1 T(\log T - 1) + (e_1)_0 - T(s_1)_0 \\ C_2 &= -k_2 T(\log T - 1) + (e_2)_0 - T(s_2)_0 \end{aligned}\right\}.$$

In this k_1 and k_2 are the capacities of heat at infinitely large constant volume, $(e_1)_0$ and $(e_2)_0$ the constants of energy, $(s_1)_0$ and $(s_2)_0$ the constants of entropy of the components.

With equilibrium between the two components we have:

$$\mu_1 - {}^1/_2\,\mu_2 = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

when μ_1 and μ_2 represent the two *molecular* potentials (viz. $\mu_1 = \dfrac{\partial Z}{\partial n_1}$ and $\mu_2 = \dfrac{\partial Z}{\partial n_2}$) of the components. [$\mu_1$ refers, therefore, in mercury to 200,6 Gr., μ_2 on the other hand to $2 \times 200{,}6$ Gr. mercury]. Now

$$\left.\begin{aligned} \mu_1 &= C_1 - \frac{\partial \omega}{\partial n_1} + RT\,(1 + \log(n_1 + n_2)) + RT \log c_1 \\ \mu_2 &= C_2 - \frac{\partial \omega}{\partial n_2} + RT(1 + \log(n_1 + n_2)) + RT \log c_2 \end{aligned}\right\},$$

as e.g. $\dfrac{\partial}{\partial n}(n_1 \log n_1 + n_2 \log n_2) = 1 + \log(n_1 + n_2) + \log \dfrac{n_1}{n_1 + n_2} = 1 +$

[1]) Cf. among others Arch. TEYLER (2) **11**, 3ième Partie, p. 1—97 (1908).

$+ log\,(n_1 + n_2) + log\,c_1$, while ω has been written for $\int pdv - pv$. Hence (a) becomes:

$$(C_1 - {}^1/_2\,C_2) - \left(\frac{\partial\omega}{\partial n_1} - \frac{1}{2}\frac{\partial\omega}{\partial n_2}\right) + \tfrac{1}{2}RT\,(1 + log\,(n_1 + n_2)) + \tfrac{1}{2}RT\,log\,\frac{c_1^{\,2}}{c_2} = 0.$$

Further evidently $n_1 = {}^1/_2 \times 2x = x$, $n_2 = {}^1/_2\,(1 - x)$, because from 1 single molecule $= {}^1/_2$ double molecule arise ${}^1/_2\,(1-x)$ double molecules and ${}^1/_2 \times 2x$ single molecules.

Now $\frac{\partial\omega}{\partial x} = \frac{\partial\omega}{\partial n_1}\frac{dn_1}{dx} + \frac{\partial\omega}{\partial n_2}\frac{dn_2}{dx} = \frac{\partial\omega}{\partial n_1} - \frac{1}{2}\frac{\partial\omega}{\partial n_2}$, so that we get:

$$(C_1 - {}^1/_2\,C_2) - \frac{\partial\omega}{\partial x} + \tfrac{1}{2}\,RT\,(1 + log\,\tfrac{1}{2}\,(1 + x)) + \tfrac{1}{2}\,RT\,log\,\frac{c_1^{\,2}}{c_2} = 0,$$

i.e.

$$\frac{1}{2}\,log\,\frac{c_1^{\,2}}{c_2} = \frac{\frac{1}{2}C_2 - C_1}{RT} + \frac{\frac{\partial\omega}{\partial x}}{RT} - \tfrac{1}{2}\,(1 + log\,\tfrac{1}{2}\,(1 + x)) \quad . \quad . \quad . \quad (b)$$

From $p = \frac{{}^1/_2\,(1 + x)\,RT}{v - b} - \frac{a}{v^2}$ follows for $\omega = \int pdv - pv$ [in which in $\int pdv$ x must be kept constant, because in the original equation for Z (which holds for *any* mixture, whether in equilibrium or not) the later possible state of equilibrium of the components, given by (a), must not be taken into account, so that n_1 and n_2, hence x remain constant]:

$$\omega = \tfrac{1}{2}\,(1 + x)\,RT\left[log\,(v - b) + \int\limits_{(x=konst.)}\frac{db}{v - b}\right] + \frac{a}{v} - pv.$$

In general b is still a function of v, hence in $\int pdv$ the part $\int\frac{dv}{v-b}$ will be represented by $\int\frac{d\,(v-b)}{v-b} + \int\frac{db}{v-b} = log\,(v-b) + \int\frac{db}{v-b}$.

[We may point out that in the assumed equation of state the quantities v, a, and b of the mixture refer to simple molecular quantities (e g. 200,6 Gr. mercury). For with $v' = nv$, $b' = nb$, $a' = n^2a$, in which n is the degree of association $2 : (1 + x)$, the original equation $p = \frac{RT}{v' - b'} - \frac{a'}{v'^2}$ (cf. the first part of this paper) passes into the given equation. If e.g. ${}^1/_2\,(2x)$ simple and ${}^1/_2\,(1-x)$ double molecules arise from 1 single $= {}^1/_2$ double molecule, then

$b = xb_1 + {}^1/_2(1-x)\,b_2$ — when b_1 represents the co-volume of 1 single molecule and b_2 that of 1 double molecule — which quantity refers, therefore, to the original single-molecular quantity. But b' refers to the molecular quantity, which on an average yields 1 molecule after the association, and which is $2:(1+x)$ times greater than the single-molecular quantity. [i.e. at $x=0$ (exclusively double molecules) twice greater; at $x=1$ (exclusively single molecules) once greater; etc.]. For from the original single molecule there have been formed ${}^1/_2(1+x)$ new molecules, so that every new molecule corresponds averagely to $2:(1+x)$ original single molecules].

We can now compute $\frac{\partial\omega}{\partial x}$. As b is a function of v (through b_1 and b_2) and of x, and also v a function of x on account of the equation of state $v = f(p, T, x, a, b)$, in which also a and b are functions of x, we have:

$$\frac{d}{dx}\left(log(v-b)+\theta\right) = \frac{1}{v-b}\left[\frac{dv}{dx} - \left(\frac{\partial b}{\partial v}\right)_x \frac{dv}{dx} - \left(\frac{\partial b}{\partial x}\right)_v\right] + \left[\frac{1}{v-b}\left(\frac{\partial b}{\partial v}\right)_x \frac{dv}{dx} + \left(\frac{\partial\theta}{\partial x}\right)_v\right],$$

when θ is written for $\int\limits_{x=const.} \frac{db}{v-b} = \int\limits_{x=const.} \frac{\frac{db}{dv}}{v-b}\,dv$, aud because evidently $\left(\frac{\partial\theta}{\partial v}\right)_v = \frac{1}{v-b}\left(\frac{\partial b}{\partial v}\right)_x$. Hence

$$\frac{d}{dx}\left(log\ (v-b)+\theta\right) = \frac{1}{v-b}\frac{dv}{dx} - \frac{1}{v-b}\left(\frac{\partial b}{\partial x}\right)_v + \left(\frac{\partial\theta}{\partial x}\right)_v.$$

For the further calculation of $\left(\frac{\partial\theta}{\partial x}\right)_v$ the quantity θ must be known, i. e. b in function of v. When we assume for this the approximate relation derived by me before [1]):

$$\frac{v-b}{v-b_0} = \beta\frac{b}{b_0},$$

in which β is a coefficient that depends on the nature of the substance, then $\left(\frac{\partial b}{\partial v}\right)_x = \frac{(1-\beta)\,b_0^2}{N^2}$ and $v-b = \frac{\beta v\,(v-b_0)}{N}$ easily follows from $b = \frac{b_0 v}{\beta v + (1-\beta)b_0}$. In consequence of this θ becomes:

$$\theta = \int\limits_{x=const} \frac{(1-\beta)\,b_0^2}{\beta v\,(v-b_0)\,(\beta v + (1-\beta)\,b_0)}\,dv = \int\left[\frac{\beta}{\beta v + (1-\beta)b_0} - \frac{{}^1/_\beta}{v} + \frac{{}^1/_\beta - 1}{v-b_0}\right]dv,$$

[1]) See Recueil des Trav. Chim. N°. 3 and 5 of 1920.

i.e.

$$\theta = log\,(\beta v + (1-\beta)\,b_0) - \frac{1}{\beta}\,log\,v + \frac{1-\beta}{\beta}\,log\,(v-b_0),$$

which properly becomes $= 0$ for $\beta = 1$ (ideal substances, where b is independent of v).

For this may also be written, because (see above) $\beta v + (1-\beta)b_0 = \frac{b_0 v}{b}$:

$$\theta = log\frac{b_0 v}{b} - \frac{1}{\beta}\,log\,v + \frac{1-\beta}{\beta}\,log\,(v-b_0) = -\frac{1-\beta}{\beta}\,log\frac{v}{v-b_0} - log\frac{b}{b_0}.$$

Now $v = \frac{(1-\beta)b}{1-\beta\,{}^{b}/_{b_0}}$, hence $v-b_0 = \frac{b-b_0}{1-\beta\,{}^{b}/_{b_0}}$, and θ becomes:

$$\theta = -\frac{1-\beta}{\beta}log\frac{(1-\beta)b}{b-b_0} - log\frac{b}{b_0} = \frac{1-\beta}{\beta}log\,(b-b_0) - \frac{1}{\beta}logb + logb_0 - \frac{1-\beta}{\beta}log(1-\beta).^{1})$$

Thus we find for $\left(\frac{\partial\theta}{\partial x}\right)_v$:

$$\left(\frac{\partial\theta}{\partial x}\right)_v = \frac{1-\beta}{\beta}\frac{1}{b-b_0}\left(\left(\frac{\partial b}{\partial x}\right)_v - \left(\frac{\partial b_0}{\partial x}\right)_v\right) - \frac{1}{\beta}\frac{1}{b}\left(\frac{\partial b}{dx}\right)_v + \frac{1}{b_0}\left(\frac{\partial b_0}{\partial x}\right)_v,$$

or also:

$$\left(\frac{\partial\theta}{\partial x}\right)_v = \frac{{}^{b_0}/_{\beta}-b}{b\,(b-b_0)}\left(\frac{\partial b}{\partial x}\right)_v - \frac{{}^{b_0}/_{\beta}-b}{b_0\,(b-b_0)}\left(\frac{\partial b_0}{\partial x}\right)_v.$$

Now $v-b = b\,(b-b_0) : ({}^{b_0}/_{\beta}-b)$ (see the note), hence finally:

$$\left(\frac{\partial\theta}{\partial x}\right)_v = \frac{1}{v-b}\left(\frac{\partial b}{\partial x}\right)_v - \frac{b}{b_0}\frac{1}{v-b}\left(\frac{\partial b_0}{\partial x}\right)_v.$$

For $\frac{d}{dx}\,(log\,(v-b) + \theta)$ may therefore simply be written $\frac{1}{v-b}\,\frac{dv}{dx} - \frac{b}{b_0}\,\frac{1}{v-b}\left(\frac{\partial b_0}{\partial x}\right)_v$, i.e. $\frac{1}{v-b}\,\frac{dv}{dx} - \frac{b}{b_0}\,\frac{\Delta b_0}{v-b}$. For as $b_0 = x\,(b_1)_0 + {}^1/_2\,(1-x)\,(b_2)_0$, we have $\left(\frac{\partial b_0}{\partial x}\right)_v = (b_1)_0 - {}^1/_2\,(b_2)_0$, which quantity we shall represent by Δb_0. This is accordingly the increase of volume, when ${}^1/_2$ double molecule passes into 1 single molecule. From the above given expression

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1) In $\theta = \int\frac{db}{v-b}$ we might at once have substituted $v - b = b\,\frac{\beta({}^{b}/_{b_0}-1)}{1-\beta\,{}^{b}/_{b_0}}$ (derived from the above given expression for v) for $v - b$, and

$$\theta = \int\frac{b_0-\beta b}{\beta b(b-b_0)}\,db = \int\left(\frac{{}^1/_{\beta}-1}{b-b_0} - \frac{{}^1/_{\beta}}{b}\right)db = \left(\frac{1}{\beta}-1\right)log\,(b-b_0) - \frac{1}{\beta}\,log\,b$$

might have been written, but then the constant term (i.e. constant with regard to v) $log\,b_0$, essential for the differentiation with respect to x, would have been wanting, and θ would not have become $= 0$ for $\beta = 1$ (the integral is indefinite).

for ω we now find for $\frac{d\omega}{dx}$:

$$\frac{d\omega}{dx} = \tfrac{1}{2} RT\,[log\,(v-b+\theta] + \tfrac{1}{2}(1+x)\,RT\left[\frac{1}{v-b}\frac{dv}{dx} - \frac{b}{b_0}\frac{\Delta b_0}{v-b}\right] - \\ - \frac{a}{v^2}\frac{dv}{dx} + \frac{1}{v}\frac{da}{dx} - p\frac{dv}{dx}.$$

In this all the terms with $\frac{dv}{dx}$ are eliminated in consequence of the equation of state, and we keep:

$$\frac{1}{RT}\frac{d\omega}{dx} = \tfrac{1}{2}\,[log\,(v-b) + \theta] - \tfrac{1}{2}(1+x)\,\frac{b}{b_0}\frac{\Delta b_0}{v-b} + \frac{1}{RTv}\frac{da}{dx}.$$

With regard to the quantity a, the following equation may be given:

$\sqrt{a} = x\sqrt{a_1} + {}^1/_2(1-x)\sqrt{a_2} = {}^1/_2\sqrt{a_2} + x(\sqrt{a_1} - {}^1/_2\sqrt{a_2}) = {}^1/_2\sqrt{a_2} + x\Delta\sqrt{a}$, when $\sqrt{a_1}$ refers to one single molecule and $\sqrt{a_2}$ to one double molecule, and $\Delta\sqrt{a}$ represents the *increase* of the attraction, when ${}^1/_2$ double molecule passes into 1 single molecule (atom). As for mercury ${}^1/_2\ \sqrt{a_2}$ is about $= 10 \,.\, 10^{-2}$ and $\sqrt{a_1}$ about $= 40 \,.\, 10^{-2}$, $\Delta\sqrt{a}$ has there the exceedingly high value $30.\,10^{-2}$, i.e. $\Delta\sqrt{a}$ three times the value of $\sqrt{a_2}$.

Hence from $a = (\sqrt{a})^2$ follows $^{da}/_{dx} = 2\sqrt{a}\,.\,\Delta\sqrt{a}$, and thus the equation (b) becomes finally:

$$\frac{1}{2}log\frac{x^2}{1-x^2} = C + \frac{1}{2}\left[log\,\frac{v-b}{{}^1/_2(1+x)} + \theta\right] - \tfrac{1}{2}(1+x)\frac{b}{b_0}\frac{\Delta b_0}{v-b} + \frac{2\sqrt{a}\,.\,\Delta\sqrt{a}}{RTv}, \quad (c)$$

when we combine $\frac{{}^1/_2\,C_2 - C_1}{RT} - \tfrac{1}{2} - log\ 2$ to one constant (temperature function) C_1, and write for c_1 and c_2 resp. $c_1 = x : {}^1/_2(1+x)$ and $c_2 = {}^1/_2\,(1-x) : {}^1/_2\,(1+x)$.

It is now this last equation that serves as basis for the determination of the degree of dissociation x of the double molecules, i. e. for the determination of the quantity $\frac{dx}{dv}$, which will occur in the expressions for $\frac{dp}{dv}$ and $\frac{d^2p}{dv^2}$. In the equation mentioned the quantity Δb_0 will probably be always exceedingly small, and may be neglected in most cases, whereas on the contrary in this special case, where the dissociation of the double molecules Hg_2 leads to *isolated atoms Hg*, $\Delta\sqrt{a}$ will possess a very large value, which quite governs the modification of the critical quantities.

§ 10. Determination of $\left(\frac{dx}{dv}\right)_t$.

Let us now differentiate the relation (*c*), i.e. $x = f(v,T)$ at T constant with respect to v, again taking into account that $b = f(v,x)$ and $a = f(x)$. We then get:

$$\frac{1}{2}\left(\frac{2}{x}+\frac{2x}{1-x^2}\right)\frac{dx}{dv} = \frac{1}{2}\left[\frac{1}{v-b}\left\{1-\left(\frac{\partial b}{\partial v}\right)_x-\left(\frac{\partial b}{\partial x}\right)_v\frac{dx}{dv}\right\}+\right.$$

$$\left.+\left\{\left(\frac{\partial\theta}{\partial v}\right)_x+\left(\frac{\partial\theta}{\partial x}\right)_v\frac{dx}{dv}\right\}\right]-\tfrac{1}{2}\frac{1}{1+x}\frac{dx}{dv}-$$

$$-\frac{1}{2}\left[\frac{\Delta b_6}{\beta(v-b_0)}\frac{dx}{dv}+\frac{(1+x)\,\Delta b_0}{\beta}\frac{d}{dv}\left(\frac{1}{v-b_0}\right)\right]-\frac{2\sqrt{a}.\Delta\sqrt{a}}{RTv^2}+\frac{2(\Delta\sqrt{a})^2}{RTv}\frac{dx}{dv},$$

because $\frac{1}{\beta(v-b_0)}$ can also be written for $\frac{b}{b_0}\frac{1}{v-b}$ (see § 9). As further

$$\left(\frac{\partial\theta}{\partial v}\right)_x=\frac{1}{v-b}\left(\frac{\partial b}{\partial v}\right)_x \text{ and } \left(\frac{\partial\theta}{\partial x}\right)_v=\frac{1}{v-b}\left(\frac{\partial b}{\partial x}\right)_v-\frac{b_0}{\beta(v-b_0)} \text{ (see § 9),}$$

we get:

$$\left(\frac{1}{x(1-x^2)}+\frac{1}{2}\frac{1}{1+x}\right)\frac{dx}{dv}=\frac{1}{2}\left[\frac{1}{v-b}-\frac{\Delta b_0}{\beta(v-b_0)}\frac{dx}{dv}\right]-$$

$$-\frac{1}{2}\left[\frac{\Delta b_0}{\beta(v-b_0)}\frac{dx}{dv}-\frac{(1+x)\,\Delta b_0}{\beta}\frac{1-\Delta b_0\frac{dx}{dv}}{(v-b_0)^2}\right]-\frac{2\sqrt{a}.\Delta\sqrt{a}}{RTv^2}+\frac{2(\Delta\sqrt{a})^2}{RTv}\frac{dx}{dv},$$

or also

$$\left.\begin{aligned}\left[1+\tfrac{1}{2}x(1-x)+\frac{\Delta b_0}{\beta(v-b_0)}+\frac{(1+x)(\Delta b_0)^2}{\beta(v-b_0)^2}-\frac{2(\Delta\sqrt{a})^2}{RTv}\right]\frac{dx}{dv}=\\ =\frac{1}{2}\frac{1}{v-b}+\frac{1}{2}\frac{(1+x)\,\Delta b_0}{\beta(v-b_0)^2}-\frac{2\sqrt{a}.\Delta\sqrt{a}}{RTv^2}\end{aligned}\right\}.$$

When to obviate unnecessary complications in what follows, we disregard all the terms with Δb_0 — which may the sooner be done, as at the *limiting volume* $v_0 = b_0$ the volume of $\frac{1}{2}$ double molecule will probably be equal to that of 1 single molecule, and as besides $\Delta\sqrt{a}$ is very large with regard to Δb_0 — we thus get:

$$\left(\frac{dx}{dv}\right)_t=\frac{\frac{1}{2}\frac{1}{v-b}-\frac{2\sqrt{a}.\Delta\sqrt{a}}{RTv^2}}{\frac{1+\frac{1}{2}x(1-x)}{x(1-x^2)}-\frac{2(\Delta\sqrt{a})^2}{RTv}},$$

i.e.

$$\left(\frac{dx}{dv}\right)_t = \frac{1}{v-b} \frac{{}^1/_2 x(1-x)\left(1 - \frac{v-b}{v}\frac{4\sqrt{a}\,.\,\Delta\sqrt{a}}{RTv}\right)}{(1-{}^1/_2 x) - 2x(1-x)(\Delta\sqrt{a})^2 : RTv} =$$

$$= \frac{1}{v-b} \frac{x(1-x)\left(RTv - 4\frac{v-b}{v}\sqrt{a}\,.\,\Delta\sqrt{a}\right)}{(2-x)\,RTv - 4x(1-x)(\Delta\sqrt{a})^2},$$

because $1 + {}^1/_2 x(1-x) : (1+x)$ is $= 1-{}^1/_2 x$. If we put for brevity:

$$\frac{v-b}{v}\sqrt{a} = \alpha \quad \text{and} \quad \Delta\sqrt{a} = \Delta,$$

we have finally:

$$\left(\frac{dx}{dv}\right)_t = \frac{1}{v-b} \frac{x(1-x)(RTv - 4\alpha\Delta)}{(2-x)\,RTv - 4x(1-x)\Delta^2} \quad \ldots \quad (1)$$

When $\Delta = 0$, or may be neglected, as in all cases of dissociation which do *not* eventuate in isolated atoms, then $\left(\frac{dx}{dv}\right)_t = \frac{1}{v-b}\frac{x(1-x)}{2-x}$, the already known expression, which is always positive, and which becomes $= 0$ for $x = 0$ and $x = 1$.

But if Δ is large, as with $Hg_2 \rightarrow 2\,Hg$, then in consequence of $RTv - 4\alpha\Delta = RTv - 4\frac{v-b}{v}\sqrt{a}\,.\,\Delta\sqrt{a} = v\left[RT - 4\frac{a}{v}\frac{v-b}{v}\frac{\Delta\sqrt{a}}{\sqrt{a}}\right]$ the quantity ${}^{dx}/_{dv}$ can become *negative* at lower temperatures or comparatively small values of v. In mercury, where $\sqrt{a} = {}^1/_2\sqrt{a_2} + x\,.\,\Delta\sqrt{a}$ is $= (10 + 30x)\,.\,10^{-2}$, $\Delta\sqrt{a} : \sqrt{a}$ will approach $30 : 10 = 3$ with small values of x, so that then the transition from positive to negative is reached, when $RT = 12\frac{a}{v}\frac{v-b}{v}$. If $v = v_c$, then with $v_c = 1{,}8\,b_c$, and a about $= {}^3/_4\,a_c$, $b = {}^3/_4\,b_c$, this temperature will be given by $RT = 12 \times \frac{0{,}75}{1{,}8}\frac{a_c}{b_c}\frac{1{,}8-0{,}75}{1{,}8} = \frac{35}{12}\frac{a_c}{b_c}$. And as in mercury RT_c is $\frac{8}{27}\frac{a_c}{b_c} \times 2 \times (\text{about } 1{,}25) = \frac{20}{27}\frac{a_c}{b_c}$ (compare the first part in these Proc.), T becomes about $= {}^{63}/_{16}\,T_c$, i.e.

$$T \sim 4\,T_c \,(\text{at } v = v_c),$$

so that with a volume $= v_c$ the quantity ${}^{dx}/_{dv}$ becomes positive again only above about 6700° abs.

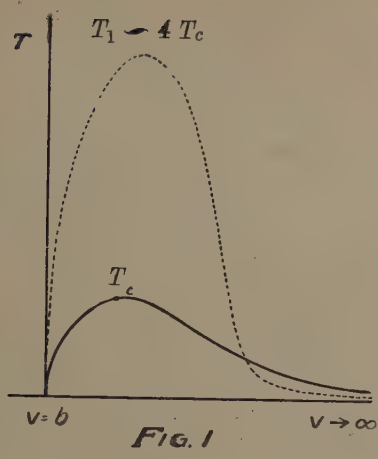

FIG. 1

Hence $^{dx}/_{dv}$ is always *negative* at the *critical temperature itself*, when $\Delta\sqrt{a}$ has such a high value as in mercury and similar substances. Then the degree of dissociation of the double molecules Hg_2 *decreases* when the volume becomes greater, instead of increasing — as it generally does.

As $a(v-b):v^2$ (a and b assumed constant) has its maximum value at $v = 2b$, the transition temperature for values of v both about $< 2b$ and $> 2b$ will be lower than that (T_1) at $v = 2b$, which latter will be only little higher than that at $v = v_c$ (about $4\,T_c$) [1]). See fig. 1.

The decrease of x with increasing volume is of course accounted for in this way, that on increase of the degree of dissociation x with increasing volume also a becomes greater. But this causes the volume to decrease again, in which the decrease in the end exceeds the original increase.

At high temperature the pressure will be comparatively great, so that then, in consequence of an increase of a, $p + {}^{a}/_{v^2}$ will be increased little; $v-b$, hence also v, will then be lowered comparatively little. For this reason $^{dx}/_{dv}$ will always be positive at high

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[1]) The righthand branch of the transition curve (dotted in the figure) will get more to the left, and T_1 possibly *slightly* lower than would follow from the above calculation, because then x can no more be assumed near 0. The intersection with the vapour branch of the saturation curve takes place at $T =$ about $0{,}8\,T_c$. For from $pv = {}^1/_2(1+x)\,RT$ and $p = p_c\,e^{-4{,}14(1/m\,-1)}$, where 4,14 is the vapour pressure factor $f = 1{,}8 \times 2{,}303$ and $m = T:T_c$, follows $p_c\,v\,e^{-etc.} = {}^1/_2\,(1+x)\,mRT_c$. When x is put approximately $= {}^1/_2$, then $n\,e^{-etc.}$ becomes $= {}^3/_4\,m\,s$. (with $v = nv_c$ and $RT_c : p_c v_c = s$). Now in mercury $s = 2{,}62$ (see the cited first part), so that finally $n = 1{,}965\,m\,e^{4{,}14(1/m\,-1)}$ (saturation curve). This must now be combined with $RT = 4\,\frac{a}{v}\,\frac{v-b}{v}\,\frac{\Delta\sqrt{a}}{\sqrt{a}}$. In this $\Delta\sqrt{a} = 30\,.\,10^{-2}$, while $\sqrt{a}$ becomes $= 25{,}10^{-2}$ with $x = {}^1/_2$. When at the point of intersection a is put about $= 1{}^1/_4\,a_c$, $b = 1{}^1/_4\,b_c$, then $mRT_c = 6\,\frac{a_c}{nv_c}\,\frac{nv_c - 1{}^1/_4 b_c}{nv_c}$, i. e. with $v_c = 1{,}8\,b_c$ and $RT_c = \frac{20}{27}\,\frac{a_c}{b_c}$ (see above) $m = 2{,}5\,\frac{1{,}8n - 1{}^1/_4}{n^2}$ (transition curve). Both equations are satisfied by $m = 0{,}778$, $n = 4{,}99$ (point of intersection), so that this will lie at about $T = 0{,}8\,T_c$, where $v = 5v_c$.

temperatures (higher than the critical transition temperature $T_1, = 4T_c$ in *Hg*). The same thing is also the case with great values of v, for then a/v^2 has only slight influence by the side of p.

As regards the values of v near b, here too dx/dv will always be positive, because v cannot become smaller than b, and x not smaller than 0. In consequence of the increase of a the volume will indeed become somewhat smaller; but this decrease can only be exceedingly small, as v is already almost $= b$.

Remark. In the equation (*c*) the constant C will contain the term $(1/2\,(e_2)_0 - (e_1)_0) : RT = -Q_0 : RT$ (on account of $(1/2\,C_2 - C_1) : RT$), in which Q_0 represents the — always positive — heat of dissociation (see § 9), while θ contains the term $(1/\beta - 1)\,log\,(v-b)$ (for $v - b = (v - b_0) \times \beta\, b/b_0$); hence $x : \sqrt{1-x^2}$ will have the form $k \times (v-b)^{1/2\beta} \times e^{\left(-Q_0 + \frac{2\sqrt{a}\,.\,\Delta\sqrt{a}}{v}\right) : RT}$, in which k will contain exponentially neither $v-b$ nor T. If, therefore, the term with $\Delta\sqrt{a}$ is smaller than Q_0, then x will approach 0 exponentially at $T=0$, $v = b$. (If the term with $\Delta\sqrt{a}$ should be larger than Q_0, $1-x$ approaches 0 exponentially). Hence according to (1) the differential quotient dx/dv will approach exponentially to 0 at any rate at $T=0$, $v = b$, as it contains the factor $x\,(1-x) : (v-b)$. If, however, T is > 0, everything depends at $v = b$ on the exponent of $v-b$, which will evidently be $1/2\beta - 1$. In "ideal" substances, where $\beta = 1$, this exponent is negative, hence dx/dv approaches to ∞. But for "ordinary" substances, in which $1/\beta$ ranges between a little more than 2 and a little more than 4 (according as, in view of the factor $1 : a$ occurring in β, the temperature is higher or lower), the exponent in question will be positive, and dx/dv will thus approach 0.

§ 11. The Differential Quotient $\left(\frac{dp}{dv}\right)_t$ and the Value of RT_c.

From the equation of state $p = \frac{1/2\,(1+x)\,RT}{v-b} - \frac{a}{v^2}$ follows:

$$\left(\frac{dp}{dv}\right)_t = \frac{1/2\,RT}{v-b}\left(\frac{dx}{dv}\right)_t - \frac{1/2\,(1+x)\,RT}{(v-b)^2}\left(1 - \left(\frac{\partial b}{\partial v}\right)_x - \left(\frac{\partial b}{\partial x}\right)_v\left(\frac{dx}{dv}\right)_t\right) +$$

$$+ \frac{2a}{v^3} - \frac{2\sqrt{a}\,.\,\Delta\sqrt{a}}{v^2}\left(\frac{dx}{dv}\right)_t.$$

Putting again $\left(\frac{\partial b}{\partial x}\right)_c = \Delta b = 0$, just as before Δb_0, and writing

b' for $\left(\frac{\partial b}{\partial v}\right)_x$, we get:

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{2}\left(\frac{dx}{dv}\right)_t \left[\frac{RT}{v-b} - \frac{4\sqrt{a}\,.\,\Delta\sqrt{a}}{v^2}\right] - \frac{{}^1/_2\,(1+x)\,RT}{(v-b)^2}(1-b') + \frac{2a}{v^3}.$$

Now substituting for $^{dx}/_{dv}$ its value from (1), we find:

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{2}\,\frac{x(1-x)}{v-b}\,\frac{RTv - 4a\Delta}{(2-x)\,RTv - 4x(1-x)\,\Delta^2}\left[\frac{RT}{v-b} - \frac{4a\Delta}{v(v-b)}\right] -$$

$$- \frac{{}^1/_2\,(1+x)\,RT}{(v-b)^2}(1-b') + \frac{2a}{v^3},$$

writing simply $a\,{}^v/_{v-b}$ for $\sqrt{a}$ (see § 10) and Δ for $\Delta\sqrt{a}$; hence also:

$$\left(\frac{dp}{dv}\right)_t = \frac{1}{2v(v-b)^2}\left[\frac{x(1-x)\,(RTv-4a\Delta)^2}{(2-x)\,RTv - 4x(1-x)\,\Delta^2} - (1+x)\,RTv\,(1-b') + 4a^2\right].$$

This must now be $= 0$ at the critical point; thus we have:

$x(1-x)\,(RTv-4a\Delta)^2 = [(2-x)RTv - 4x(1-x)\,\Delta^2]\,[(1+x)\,RTv)\,1-b') - 4a^2]$,

i.e. after some reduction and division of the two members by RTv:

$$x(1-x)\,RTv - 8x(1-x)\,a\Delta = (2-x)(1+x)\,RTv\,(1-b') - 4(2-x)\,a^2 -$$

$$- 4x(1-x^2)(1-b')\,\Delta^2,$$

and from this:

$$\underline{\tfrac{1}{4}\,RT_c v_c} = \frac{(2-x)\,a^2 - 2x(1-x)\,a\Delta + x(1-x^2)(1-b')\,\Delta^2}{(2-x)(1+x)(1-b') - x(1-x)}, \quad (2)$$

for which we may also write:

$$\tfrac{1}{4}\,RT_c\,v_c = a\Delta + \frac{(a - (1+x)(1-b')\,\Delta)\,((2-x)\,a - x(1-x)\,\Delta)}{(2-x)(1+x)(1-b') - x(1-x)}. \quad (2a)$$

This is, therefore, already the expression for RT_c, expressed in v_c, b_c, etc. As a check may serve that at $\Delta = 0$ this passes into

$$RT_c = \frac{4(2-x)\,a^2}{Nv_c} = \frac{4(2-x)\,a_c}{N}\,\frac{(v_c-b_c)^2}{v_c^3},$$

our former expression (Arch. Teyler loc. cit.), derived for the case that there does not take place any change in the molecular attraction in consequence of the dissociation of the double molecules.

If also $x = 1$ (all the molecules single), then becomes

$$RT_c = \frac{2a_c}{1-b'_c}\,\frac{(v_c-b_c)^2}{v_c^2} = \frac{2}{1-b'_c}\,\frac{(r-1)^2}{r^3}\,\frac{a_c}{b_c},$$

as we also found before. (Cf. among others These Proc. Vol. XVI, p. 45, and Ibid., p. 810). In this the value of $r = v_c : b_c$ can of course not be determined until we have also put $\left(\frac{d^2p}{dv^2}\right)_t = 0$.

In ideal substances $b'_c = 0$, $r = 3$, hence $RT_c = \frac{8}{27}\,\frac{a_c}{b_c}$. In ordinary

substances, where b'_c approaches $^1/_8$ and r approaches 2, RT'_c becomes $= \frac{8}{28}\frac{a_c}{b_c}$; both known expressions.

We will now first substitute the found value of RT_c in (1), in order to determine the value of $^{dx}/_{dv}$ at the critical point. If we write for brevity:

$$\left.\begin{array}{l} \alpha - (1+x)(1-b')\,\Delta = A \;;\quad (2-x)\,\alpha - x\,(1-x)\,\Delta = B \\ (2-x)(1+x)(1-b') - x\,(1-x) = 2 - (2-x)(1+x)\,b' = N \end{array}\right\},$$

we get, after substitution of

$$\tfrac{1}{4} RT_c\, v_c = \alpha\,\Delta + \frac{AB}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

in

$$\left(\frac{dx}{dv}\right)_t = \frac{x\,(1-x)}{v-b}\,\frac{^1/_4\,RTv - \alpha\,\Delta}{(2-x)\,^1/_4\,RTv - x\,(1-x)\,\Delta^2},$$

the equation

$$\left(\frac{dx}{dv}\right)_t = \frac{x\,(1-x)}{v-b}\,\frac{AB:N}{(2-x)\,\alpha\,\Delta + (2-x)\,AB:N - x\,(1-x)\,\Delta^2}.$$

In this $(2-x)\alpha\,\Delta - x\,(1-x)\,\Delta^2 = B\Delta$, hence also

$$\left(\frac{dx}{dv}\right)_t = \frac{x\,(1-x)}{v-b}\,\frac{A}{N\Delta + (2-x)\,A} = \frac{x\,(1-x)}{v-b}\,\frac{A}{B},$$

because $N\Delta + (2-x)\,A$ is evidently $= B$. Hence we have now for $\left(\frac{dx}{dv}\right)_t$ at the critical point the exceedingly simple expression

$$\underline{\left(\frac{dx}{dv}\right)_t}_c = \frac{x\,(1-x)}{v_c-b_c}\,\frac{A}{B} = \frac{x\,(1-x)}{v_c-b_c}\,\frac{\alpha - (1+x)(1-b')\,\Delta}{(2-x)\,\alpha - x\,(1-x)\,\Delta}, \quad . \quad . \quad (3)$$

in which x, b', α, and Δ all refer to T_c.

It is self-evident that it is unnecessary to derive an expression for p_c, as it follows immediately from the equation of state after substitution of the obtained value of RT_c. (Compare the first paper).

§ 12. The Second Differential Quotient $\left(\frac{d^2p}{dv^2}\right)_t$ and the Value of $r = v_c : b_c$.

As we observed already above, we cannot determine the final expression for RT_c, until also v_c has been expressed in b_c. But for this the knowledge of the second differential quotient is required, which must again be put $= 0$ at the critical point.

As $\left(\frac{dp}{dv}\right)_t = 0$ is identical with the expression (2) or (2b) derived from it, $\left(\frac{d^2p}{dv^2}\right)_t = 0$ is identical with $\frac{d}{dv}\left[{}^1/_4\, RTv - \left(\alpha\Delta + \frac{AB}{N}\right)\right] = 0$. When we take (2) instead of (2b),

$$^1/_4\, RTv\, N = (2-x)\,\alpha^2 - 2x\,(1-x)\,\alpha\Delta + x\,(1-x^2)\,(1-b')\,\Delta^2$$

should be differentiated with respect to v (T constant); which yields, when again, as in § 11, $\left(\frac{\partial b}{\partial x}\right)_v = \Delta b$ is put $= 0$, so that b is only a function of v:

$$\tfrac{1}{4} RT(N + N'v) = 2(2-x)\,\alpha\alpha' - \alpha^2\left(\frac{dx}{dv}\right)_t - 2x(1-x)\,\alpha'\Delta + 2(2x-1)\,\alpha\Delta\left(\frac{dx}{dv}\right)_t -$$

$$- x(1-x^2)\,b''\Delta^2 - (3x^2-1)(1-b')\,\Delta^2\left(\frac{dx}{dv}\right)_t.$$

After multiplication by v and substitution for ${}^1/_4\, RTv$ of its value (2b), we get:

$$\left(\alpha\Delta + \frac{AB}{N}\right)\left(N + x(1-x)(2x-1)\frac{v}{v-b}\, b'\frac{A}{B} - (2-x)(1+x)\,b''v\right) =$$

$$= 2\alpha' v B - v\left(\frac{dx}{dv}\right)_t\left[\alpha^2 - 2(2x-1)\alpha\Delta + (3x^2-1)(1-b')\Delta^2\right] - x(1-x^2)b''v\Delta^2.$$

For from $N = 2 - (2-x)(1+x)\,b'$ follows $N' = -(2-x)(1+x)\,b'' + (2x-1)\,b'\left(\frac{dx}{dv}\right)_t$, hence $N'v$ becomes with $\left(\frac{dx}{dv}\right)_t = \frac{x(1-x)}{v-b}\frac{A}{B}$, which is written down above. Further $(2-x)\,\alpha - x(1-x)\,\Delta$ has been replaced by B.

For $\alpha' = \left(\frac{d\alpha}{dv}\right)_t = \frac{d}{dv}\left(\frac{v-b}{v}\sqrt{a}\right)_t$ we find $\left(\frac{1-b'}{v} - \frac{v-b}{v^2}\right)\sqrt{a} + \frac{v-b}{v}\Delta\sqrt{a}\left(\frac{dx}{dv}\right)_t$, hence

$$\alpha' v = \alpha\left(\frac{v}{v-b}(1-b') - 1\right) + x(1-x)\frac{A}{B}\Delta = \alpha\frac{v}{v-b}(1-b') - \frac{1}{B}\left(\alpha B - x(1-x)A\Delta\right),$$

so that we find:

$$\left(\alpha\Delta + \frac{AB}{N}\right)\left(N + x(1-x)(2x-1)\frac{v}{v-b}\, b'\frac{A}{B}\right) -$$

$$- \frac{(1+x)\,b''v}{N}\left[(2-x)(N\alpha\Delta + AB) - x(1-x)N\Delta^2\right] =$$

$$= 2B\left[\alpha\frac{v}{v-b}(1-b') - \frac{\alpha B - x(1-x)A\Delta}{B}\right] -$$

$$- x(1-x)\frac{v}{v-b}\frac{A}{B}\left[\alpha^2 - 2(2x-1)\alpha\Delta + (3x^2-1)(1-b')\Delta^2\right].$$

When now for brevity C is written for

$$N\alpha\Delta + AB = (2-x)\alpha^2 - 2x(1-x)\alpha\Delta + x(1-x^2)(1-b')\Delta^2$$

(according to (2) and (2b)), then

$$C + x(1-x)(2x-1)\frac{v}{v-b}b'\frac{AC}{NB} - (1+x)\frac{B^2}{N}b''v =$$

$$= 2B\alpha\frac{v}{v-b}(1-b') - 2C - x(1-x)\frac{v}{v-b}\frac{A}{B}[\alpha^2 - \text{etc.}],$$

because $\alpha B - x(1-x)A\Delta$ is $= C$ and $(2-x)C - x(1-x)N\Delta^2 = B^2$.

Hence we have also:

$$3C - (1+x)\frac{B^2}{N}b''v = 2\alpha B\frac{v}{v-b}(1-b') - x(1-x)\frac{A}{B}\frac{v}{v-b}\left[(2x-1)b'\frac{C}{N} + (\alpha^2 - \text{etc.})\right].$$

For $(2x-1)b'C + N(\alpha^2 - \text{etc.})$ may be written $B^2(1-b') - A^2(x^2-4x-2)$, hence we have:

$$3C - \frac{(1+x)B^2}{N}b''v = 2\alpha B\frac{v}{v-b}(1-b') - x(1-x)\frac{A}{B}\frac{v}{v-b}\frac{B^2(1-b') - A^2(x^2-4x+2)}{N}. \quad (\alpha)$$

Before proceeding, we shall apply a control-calculation to this equation. When Δ is $= 0$, then A becomes $= \alpha$, $B = (2-x)\alpha$, $C = (2-x)\alpha^2$, so that then (α) passes into

$$3(2-x)\alpha^2 - \frac{(1+x)(2-x)^2\alpha^2}{N}b''v = 2(2-x)\alpha^2\frac{v}{v-b}(1-b') -$$

$$- \frac{x(1-x)}{2-x}\frac{v}{v-b}\frac{(2-x)^2\alpha^2(1-b') - \alpha^2(x^2-4x+2)}{N},$$

i.e. after division by $(2-x)\alpha^2$:

$$3 - \frac{(1+x)(2-x)}{N}b''v = 2\frac{v}{v-b}(1-b') - x(1-x)\frac{v}{v-b}\frac{(1-b') - (x^2-4x+2):(2-x)^2}{N},$$

in which $N = (2-x)(1+x)(1-b') - x(1+x) = 2 - (2-x)(1+x)b'$. This gives:

$$3 - \frac{b''v}{1-b'}\frac{1}{1 - \frac{x(1-x)}{(2-x)(1+x)(1-b')}} = \frac{v}{v-b}\left[2(1-b') - \frac{x(1-x)(1-b')}{N} + \right.$$

$$\left. + \frac{x(1-x)((2-x)^2-2)}{(2-x)^2N}\right],$$

or

$$3 - \frac{b''v}{1-b'}\frac{1}{1-\tau} = \frac{v}{v-b}\left[2(1-b') - \frac{x(1-x)}{(2-x)^2}\frac{2-(2-x)^2 b'}{2-(2-x)(1+x)b'}\right].$$

In ideal substances, where $b' = 0$, $b'' = 0$, the equation would become:

$$3 = \frac{v}{v-b}\left[2 - \frac{x(1-x)}{(2-x)^2}\right] = \frac{v}{v-b}\frac{8-9x+3x^2}{(2-x)^2},$$

identical with what we have already derived. (Arch. TEYLER and these Proc., loc. cit.).

If $x = 0$ or 1, we get:

$$3 - \frac{b''v}{1-b'} = 2\frac{v}{v-b}(1-b'),$$

and this too is a known result (These Proc., loc. cit.), which with $b' = 0$, $b'' = 0$ reduces to $3 = 2\frac{v}{v-b}$, i.e. $v_c = 3b_c$.

We shall now reduce the above equation (a) still somewhat. When we divide by $(2-x)\alpha^2$, we get the following form (see below for the meaning of τ):

$$3\left[1 - \frac{2x(1-x)}{2-x}\frac{\Delta}{\alpha} + \frac{x(1-x^2)(1-b')}{2-x}\frac{\Delta^2}{\alpha^2}\right] - \frac{(1+x)(2-x)\left(1-\frac{x(1-x)}{2-x}\frac{\Delta}{\alpha}\right)^2}{(2-x)(1+x)(1-b')(1-\tau)}b''v =$$

$$= \frac{v}{v-b}(1-b')\left[2\left(1-\frac{x(1-x)}{2-x}\frac{\Delta}{\alpha}\right) - \frac{x(1-x)}{2-x}\frac{1-(1+x)(1-b')\frac{\Delta}{\alpha}}{1-\frac{x(1-x)}{2-x}\frac{\Delta}{\alpha}} \times\right.$$

$$\left. \times \frac{(2-x)\left(1-\frac{x(1-x)}{2-x}\frac{\Delta}{\alpha}\right)^2 - \frac{x^2-4x+2}{(2-x)(1-b')}\left(1-(1+x)(1-b')\frac{\Delta}{\alpha}\right)^2}{(2-x)(1+x)(1-b')(1-\tau)}\right],$$

in which $\frac{\Delta}{\alpha} = \frac{v}{v-b}\frac{\Delta\sqrt{a}}{\sqrt{a}}$. When we now put:

$$(1+x)(1-b')\frac{\Delta}{\alpha} = \varrho \quad ; \quad \frac{x(1-x)}{2-x}\frac{\Delta}{\alpha} = \sigma \quad ; \quad \frac{x(1-x)}{(2-x)(1+x)(1-b')} = \tau,$$

so that $\sigma = \tau\varrho$, the above becomes:

$$3(1 - 2\sigma + \varrho\sigma) - \frac{(1-\sigma)^2}{1-\tau}\frac{b''v}{1-b'} =$$

$$= \frac{v-b}{v}(1-b')\left[2(1-\sigma) - x(1-x)\frac{1-\varrho}{1-\sigma}\frac{(1-\sigma)^2 - \frac{x^2-4x+2}{(2-x)^2(1-b')}(1-\varrho)^2}{(2-x)(1+x)(1-b')(1-\tau)}\right],$$

or

$$3\,(1+\tau\varrho\,(\varrho-2))-\frac{(1-\sigma)^3}{1-\tau}\,\frac{b''v}{1-b'}=$$

$$=\frac{v}{v-b}\,(1-b')\left[2\,(1-\sigma)-\frac{\tau}{1-\tau}\,\frac{1-\varrho}{1-\sigma}\right\}(1-\sigma)^2-\frac{x^3-4x+2}{(2-x)^3\,(1-b')}\,(1-\varrho)^3\Big\}\Big].$$

When further $\frac{\Delta\sqrt{a}}{\sqrt{a}}=\varphi$ is put, then $\frac{\Delta}{\alpha}=\varphi\,\frac{v}{v-b'}$, hence $\frac{v}{v-b}\times$ $\times(1-b')=\frac{\Delta}{\alpha}\,\frac{1-b'}{\varphi}=\frac{\varrho}{\varphi(1+x)}$; so that with $-\frac{b''v}{1-b'}=\beta$ and $\frac{x^3-4x+2}{(2-x)^3(1-b')}=\frac{1}{1-b'}\left(1-\frac{2}{(2-x)^2}\right)=\omega$ we get:

$$3\,(1+\tau\varrho\,(\varrho-2))+\frac{(1-\tau\varrho)^3}{1-\tau}\,\beta=$$

$$=\frac{\varrho}{\varphi\,(1+x)}\left[2\,(1-\tau\varrho)+\frac{\tau}{1-\tau}\,\frac{\varrho-1}{1-\tau\varrho}\right\}(1-\tau\varrho)^2-\omega\,(\varrho-1)^3\Big\}\Big],\quad .\quad (4)$$

when $-(\varrho-1)$ is substituted for $1-\varrho$, because ϱ is always >1. In this latter equation $\varrho=\varphi\,(1+x)\,(1-b')\times\frac{v_c}{v_c-b_c}$, being in direct connection with $r=v_c:b_c$, the principal unknown quantity; i.e. it expresses ϱ (hence $r=v_c:b_c$) in b', b'' (or β), x [1]) and the parameter $\varphi=\frac{\Delta\sqrt{a}}{\sqrt{a}}$, being in connection with, $\frac{\Delta\sqrt{a}}{{}^1/_2\sqrt{a_2}}$, as $\sqrt{a_2}={}^1/_2\sqrt{a_2}+$ $+x\Delta\sqrt{a}$. For mercury φ is therefore $=\frac{3}{1+3x}$, because then $\Delta\sqrt{a}:{}^1/_2\sqrt{a_2}=30:10=3$.

With small values of x τ is very slight; then φ is in the neighbourhood of 3, and ω in that of $1:2\ (1-b')$.

When we now express also the values of RT_c and $\left(\frac{dx}{dv}\right)_{t_c}$, found in § 11, in the auxiliary unknowns assumed just now, we may write for (2) in the first place:

$$RT_c=\frac{4}{v_c}\,\frac{(2-x)\,\alpha^2\,(1+\tau\varrho\,(\varrho-2))}{(2-x)\,(1+x)\,(1-b')\,1-\tau)}=\frac{2}{1+x}\,\frac{2\,(v_c-b_c)^2a_c}{v_c^3\,(1-b')}\,\frac{1+\tau\varrho\,(\varrho-2)}{1-\tau},$$

i.e.

$$RT_c=\frac{2}{1+x}\cdot\frac{2\,(r-1)^2}{(1-b')r^3}\,\frac{a_c}{b_c}\times\frac{1+\tau\,\varrho\,(\varrho-2)}{1-\tau},\quad .\quad .\quad .\quad .\quad (5)$$

in which $\sqrt{a_c}={}^1/_2\sqrt{a_2}+x\,\Delta\sqrt{a}={}^1/_2\sqrt{a_2}\,(1+3x)$, whilst $r=v_c:b_c$ is determined by (4).

And in the second place we may write for (3):

[1]) The value of x at the critical point will be determined by (c), and depends besides on T_c and v_c also on the constants of energy and entropy (contained in C).

$$\left(\frac{dx}{dv}\right)_t = \frac{1}{v_c - b_c}\,\frac{x\,(1-x)}{2-x}\,\frac{1-\varrho}{1-\tau\varrho}, \quad \ldots\ldots \quad (6)$$

in which $\varrho = \psi\,(1+x)\,(1-b')\,\dfrac{v_c}{v_c-b_c} = \dfrac{3\,(1+x)}{1+3x}\,(1-b')\,\dfrac{r}{r-1}$ (see above). In mercury, where $\varphi_0 = 3$, $1-\varrho$ will, therefore, always be negative at T_c, hence also dx/dv.

§ 13. Calculation of some Numerical Values.

The value of x being always very small at T_c, we way write approximately for (4), when $1-\tau = 1$ and $1+x = 1$ is put:

$$3\,(1+\tau\varrho\,(\varrho-2)) + \beta(1-\tau\varrho)^3 = \frac{\varrho}{\varphi}\left[2\,(1-\tau\varrho) + \tau\,\frac{\varrho-1}{1-\tau\varrho}\left\{(1-\tau\varrho)^3 - \omega\,(\varrho-1)^3\right\}\right],$$

and from this follows for τ $\left(= \dfrac{x}{2\,(1-b')}\right.$, when x is small (see above)$\left.\right)$:

$$\tau = \frac{\dfrac{2\varrho}{\varphi}(1-\tau\varrho) - (3+\beta\,(1-\tau\varrho)^3)}{3\varrho\,(\varrho-2) - \dfrac{1-\tau\varrho}{\varphi}\,\varrho\,(\varrho-1) + \dfrac{\omega}{1-\tau\varrho}\,\dfrac{\varrho\,(\varrho-1)^3}{\varphi}} =$$

$$= \frac{2\left[(1-\tau\varrho) - \dfrac{3+\beta\,(1-\tau\varrho)^3}{2}\,\dfrac{\varphi}{\varrho}\right]}{3\varphi\,(\varrho-2) - (1-\tau\varrho)(\varrho-1) + \dfrac{\omega}{1-\tau\varrho}\,(\varrho-1)^3}.$$

With very small values of x also $1-\tau\varrho$ can be put $= 1$, and we have approximately:

$$\tau = \frac{2\left[1 - \dfrac{3+\beta}{2\,(1-b')}\,\dfrac{r-1}{r}\right]}{3\varphi\,(\varrho-2) - (\varrho-1) + \omega\,(\varrho-1)^3}.$$

With small x we way write $1 : 2\,(1-b')$ for ω. Now ϱ is large (6 or 7), and it can easily be calculated that in the denominator the two first terms may be neglected by the side of $\omega\,(\varrho-1)^3$, provided the latter is provided with a factor about 1,35. When we also write

δ for $1 - \dfrac{3+\beta}{2\,(1-b')}\,\dfrac{r-1}{r}\left[\delta\right.$ becomes 0 at $x = 0$ $(\tau = 0)$ and $\dfrac{r}{r-1}$ is then $\left.= \dfrac{3+\beta}{2\,(1-b')}\right]$, we get:

$$\tau = \frac{2\delta}{1{,}35 \times \frac{1}{2\,(1-b')}(\varrho-1)^2}, \text{ hence } \underline{\tau\,(\varrho-1)^3 = 3\,(1-b')\,\delta.}$$

Now $1 + \tau\,(\varrho-1)^2$ may be written for the factor $(1 + \tau\varrho\,(\varrho-2)) : (1-\tau)$ in (5) for small values of τ, which in view of the above approximated relation becomes $1 + \frac{3\,(1-b')\delta}{\varrho-1}$.

Now $\varrho = 3\,(1-b')\frac{r}{r-1}$ for small values of x. This being about 6, $2{,}5\,(1-b')\frac{r}{r-1}$ may be put for $\varrho-1$, so that we get approximately $1 + \frac{6}{5}\frac{r-1}{r}\delta$ for the factor in question. Hence the factor θ in $RT_c = \frac{2}{1+x}\,\frac{8}{27}\,\frac{a_c}{b_c} \times \theta$, referred to in the first part of this paper, will evidently according to (5), when for δ its value is substituted, amount to:

$$\theta = \frac{2\,(r-1)^3}{(1-b')\,r^3} \times \frac{27}{8}\left[1 + \frac{6}{5}\,\frac{r-1}{r}\left\{1 - \frac{3+\beta}{2\,(1-b')}\,\frac{r-1}{r}\right\}\right],$$

holding for very small values for x. Only a small value of r, e.g. $r = 1{,}5$, satisfies this. If β has then become $= 0$, and $b' = {}^1/_2$, θ becomes

$$\theta = 1\left[1 + \frac{2}{5}\,(1-1)\right] = 1,$$

while with $r = 1{,}5$ (see the first part of this Paper in these Proceedings, § 8, p. 278) θ should be exactly $= 1$. Possibly x is not small enough to justify the above approximations and the neglect of certain values, and then it is possible that $r > 1{,}5$ drops out. But the calculations get very intricate then.

At any rate the formulae (4), (5), and (6) contain the full solution of the problem put by us.

La Tour près Vevey, spring 1920.

Chemistry. — *"Catalysis"* VIII. By Nil Ratan Dhar (with A. K. Datta and D. N. Bhattacharya). (Communicated by Prof. Ernst Cohen).

(Communicated at the meeting of September 25, 1920).

a. Reaction between silver nitrate and ferrous-ammonium sulphate.

I tried to determine the kinetics of the reaction between ferrous ammonium sulphate and silver nitrate. The reaction seems to be very rapid.

When $^N/_{50}$ silver nitrate and $^N/_{50}$ ferrous ammonium sulphate are mixed at 25°, a bimolecular velocity coefficient of 0.0007 is obtained, but unfortunately this coefficient falls off as the chemical reaction proceeds. Since the metallic silver formed reacts on the ferric salt produced and we get an equilibrium of this nature

$$2\,Ag + Fe_2(SO_4)_3 \rightleftarrows Ag_2SO_4 + 2\,FeSO_4$$
$$Ag + Fe(NO_3)_3 \rightleftarrows AgNO_3 + Fe(NO_3)_2$$
$$\text{or } \frac{(Fe^{++})(Ag^{+})}{Fe^{+++}} \text{ at equilibrium } = 0{\cdot}128$$

(cf. Noyes en Braun, Jour. Amer. Chem. Soc. 1912, **34**, 1016) the reaction between ferrous ammonium sulphate and silver nitrate is rapid even at 0° and has a small value for its temperature coefficient.

The reaction is markedly accelerated by acids; nitric, sulphuric, citric, tartaric, and acetic acids have been tried; the greater the concentration of hydrogen ions, the greater is the velocity. This catalytic activity may be utilised in determining the concentration of hydrogen ions.

Magnetic force has practically no effect on this reaction. It is extremely sensitive to the influence of dirt etc.

Potassium nitrate appreciably retards the reaction, so do manganese salts very markedly.

Carbonic acid markedly accelerates the reaction. Boric acid is practically without any influence. So is phenol, which is probably slightly retarding in its effect. Glucose markedly accelerates the reaction. This is a case of induced reaction. A mixture of excess of silver nitrate and very little of ferrous ammonium sulphate was prepared and divided into equal parts, to one of which glucose was

added, whilst the other was left as it is; in a short time, more silver was deposited in the tube containing glucose, though a neutral solution of glucose cannot reduce silver nitrate. This is another case of an induced reaction already studied. (Dhar, Trans. Chem. Soc. 1917, **111**, 690).

Summary: *a.* The reaction between silver nitrate and ferrous ammonium in dilute solutions is bimolecular. The reaction is very rapid even at 0° and the temperature coefficient has a small value.

b. When the chemical change has proceeded up to a certain extent, an equilibrium is set up:

$$Ag + Fe(NO_3)_3 \rightleftarrows AgNO_3 + Fe(NO_3)_2$$

c. Acids accelerate this change; in case of nitric, sulphuric, citric, tartaric acetic acids, the greater the concentration of $H^{\cdot}$ ions, the greater is the acceleration. Carbonic acid markedly accelerates, whilst boric acid and phenol are without action. Manganese sulphate and potassium nitrate are retarders.

d. A neutral solution of glucose cannot reduce silver nitrate at about 20°; the reaction between ferrous ammonium sulphate and silver nitrate induces the chemical change between glucose and silver nitrate.

b. Oxidation of sodium sulphite by atmospheric oxygen.

Luther (Zeit. phys. Chem. 1903, **45**, 662) advanced the idea that negative catalysis cannot take place in a reaction which is entirely free from positive catalysts and the phenomenon is really due to the destruction or otherwise rendering latent of these positive catalysts. Titoff (ibid. 1903, **45**, 641) as a result of his studies of the combined effect of positive and negative catalysors on the rate of oxidation of sodium sulphite lends his support to Luther's theory. The effect of negative catalysts on this reaction was first studied by Bigelow (ibid. 1898, **26**, 493), who found the oxidation of the salt in aqueous solution to be greatly retarded by the presence of minute quantities of benzaldehyde, iso-butyl alcohol, glycerol, phenol etc. Bigelow also demonstrated that the effect of negative catalyst is not on the rate of solution of oxygen, but on the rate of the reaction between the sulphite and oxygen. A few years later Titoff substantiated Bigelow's results and in addition studied the simultaneous effect produced by copper sulphate, a powerful accelerator and manitol a strong retarder. He found that these two substances do not exert any additive effect but influence each other. Young (Jour. Amer. Chem. Soc. 1901, **23**, 119; **24**, 1902, 297) found that small quantities of certain alkaloids

greatly retard this oxidation, specially if this solution is alkaline, and the inhibitory effect of sucrose, invert sugar, asparatic acid, etc., have been noted by Sailland (Zeit. Ver. Zuckerind. 1913, **63**, 1035). In 1912, we conducted some experiments on this line. From preliminary experiments it was observed that the velocity of the reactions depends greatly on the quality of the water used. Ordinary distilled water was found quite inefficient as it contained sufficient dissolved salts and gases to affect the course of the reactions materially. Freshly prepared conductivity water obtained according to the method of Jones and Mackay (Zeit. Phys. Chem. 1897, **22**, 237) was always used. The salts used were purified by recrystallisation from conductivity water and dissolved in the same water in resistance glass bottles. Well steamed Jena flasks were used as vessels in which the reaction took place. In short every care was taken to ensure purity. But in spite of all this care, it was found that velocity coefficients of the reactions carried out under identical conditions but on different days and even at different times on the same day were slightly different. Titoff also found similar results. The explanation is probably that the reaction is so susceptible to external conditions, that even the slight variation of circumstances that is inevitable when we carry out the same reaction at two different times are sufficient to affect the results. It is therefore clear that our comparison of the results tried on different days or with different concentration of the same catalyst, cannot give an accurate idea of their relative effect. To remove this difficulty, at least partially, we carried out a blank experiment in which no catalyst was added, simultaneously with the main one. Two similar Erlenmeyer flasks of capacity 150 c.c. were arranged side by side. A definite volume of sulphite was put in each flask. The catalyst was added in one flask. The course of the reaction was determined and their coefficients calculated. The ratio of these two coefficients gives the measure of the catalytic effect of the substance under consideration. In this way it was found that the ratio between the coefficients of two similar pair of reactions carried out on different days were almost the same, though their absolute velocities varied appreciably. The flasks were exposed to the atmosphere whose oxygen served as the oxidising agent.

About $\frac{N}{100}$ iodine and thio sulphate solutions were used as titration liquids. A definite volume of the sulphite solution is pipetted in a flask containing an excess of standard iodine and the excess of iodine was titrated back with the standard thio sulphate.

The temperature of the experiments was about 30° C.

Substance	Concentration	$\frac{K_1 \text{ catalyst}}{K_1 \text{ blank}}$
Cane sugar	0·2 N	0·09
"	$3\cdot1 \times 10^{-2}$ N	0·17
"	$6\cdot7 \times 10^{-3}$ N	0·47
"	$9\cdot4 \times 10^{-4}$ N	0·63
"	$3\cdot7 \times 10^{-5}$ N	0·89
Lactose	0·15 N	0·084
"	$3\cdot1 \times 10^{-2}$ N	0·15
"	$9\cdot4 \times 10^{-4}$ N	0·55
"	$3\cdot7 \times 10^{-5}$ N	0·85
Glucose	0·1 N	0·22
"	1×10^{-3} N	0·75
"	2×10^{-4} N	0·83

It will be evident from the above results that cane sugar, lactose, and glucose are very strong retarders. Cane sugar and lactose have almost similar effects, though lactose is slightly stronger in its effect.

It appears probable that sugars as a class will act as negative catalysts. It has been found that the sparingly soluble volatile substances like camphor and menthol have marked negative effect while naphthalene, anthracene etc. have no catalytic effect.

The effect of several organic acids and their salts were also investigated. (See Table next page).

It is very peculiar that the weak acids like acetic, propionic, cacodylic etc. have comparatively small retarding effects. Their sodium salts also exert practically the same effect. On the other hand comparatively strong acids like oxalic, salicylic, benzoic etc. exert much greater retarding effect, and their salts too exert the same effect as the acids. Moreover it is found that the sodium salts of stronger inorganic acid have no marked effect.

We have found that hydroquinone has a very great negative effect on this reaction. For the same concentration, it exerts the greatest negative catalytic effect amongst the negative catalysts investigated up till now. We tried to determine the temperature coefficient of this heterogeneous reaction and see whether this becomes greater in presence of the powerful negative catalyst hydroquinone. Unlike most other heterogeneous reactions, we found that the temp-

Substance	Concentration	$\frac{K_1 \text{ catalyst}}{K_1 \text{ blank}}$
Oxalic acid	$1{\cdot}2 \times 10^{-3}$ N	0 29
"	3×10^{-4} N	0·56
"	3×10^{-5} N	0·90
Benzoic acid	$1{\cdot}2 \times 10^{-3}$	0·25
"	2×10^{-4}	0·58
"	5×10^{-5}	0·83
Cacodylic acid	·02 N	0·75
"	·01 N	0·94
Sodium benzoate	1×10^{-3}	0·19
"	$0{\cdot}7 \times 10^{-3}$	0·25
"	$1{\cdot}5 \times 10^{-4}$	0·70
"	1×10^{-5}	0·90
Potassium oxalate	1×10^{-3} N	0·29
"	1×10^{-4} N	0·80
"	2×10^{-5}	0·96
Sodium salicylate	1×10^{-3}	0·23
"	$1{\cdot}5 \times 10^{-4}$	0·73
"	1×10^{-5}	0 95
Sodium citrate	1×10^{-3}	0·14
"	1×10^{-5}	0·85
Sodium acetate	3×10^{-3}	0·73
"	1×10^{-3}	0·85
Sodium propionate	3×10^{-3}	0·74
"	1×10^{-3}	0 89
Sodium butyrate	3×10^{-3}	0·74
"	1×10^{-3}	0·85

erature coefficient is about 2 (between 25°—40°) and it does not appreciably change in presence of hydroquinone (Dhar, Proc. Akad. Wet. Amsterdam 1919, 21, 1042). It has been found that so long as about one third of the substance is oxidised, the unimolecular velocity coefficient remains practically constant, but as the oxidation proceeds further, the velocity coefficient increases rapidly, and hence

it becomes very difficult to determine the temperature coefficient accurately. It appears therefore that the reaction is auto-catalytic.

Mathews and his colleagues (Jour. Phys. chem. 1913, **17**, 211; Jour. Amer. chem. Soc. 1917, **39**, 635) found that ultraviolet light markedly accelerates this reaction, and also established the fact that this is not a case of auto-oxidation. For this reaction, they could not find a positive catalyst; copper sulphate, which is known to be a powerful catalyst under ordinary conditions exerted no appreciable effect in ultra-violet light. On the other hand the negative catalysts like hydroquinone, phenol etc. exerted a retarding effect in presence of ultra-violet light. So it appears that there are very few positive catalysts, but very many negative ones for this reaction when carried out in light or darkness.

The explanation of the negative catalytic effect of organic substances in general on this reaction is this:

The reaction consists in the oxidation of SO_3 radical into SO_4, and the sulphite ion is the active agent. It is well known that several organic substances form complexes with sulphurous acid and sulphites; these complexes are stable so far as oxidation is concerned and hence the organic substances act as negative catalysts by diminishing the concentration of sulphite ion by combining with it.

In foregoing papers I have proved that the phenomenon of negative catalysis is very common, whilst there are very few positive catalysts. According to Luther's view a negative catalyst must have a positive catalyst as its counterpart, but this is not probable since there are so few positive catalysts and so many negative ones. Hence it appears that Luther's view which emphasises that negative catalysis cannot take place in a reaction which is entirely free from positive catalysts, is not substantiated by experimental evidence.

Summary.

a. Cane sugar, lactose, glucose, camphor, and menthol are negative catalysts, whilst naphthalene, and anthracene are without action on the oxidation of sodium sulphite.

b. The weak organic acids and their sodium salts exert practically the same effect. Benzoic, oxalic, salicylic acids and their sodium salts exert greater negative effect than the weak acids and their salts. It is very peculiar that the acid and its salt should exert the same effect.

c. The temperature coefficient of the reaction is about 2 and it

does not change appreciably in presence of the strong negative catalyst hydroquinone.

d. The phenomenon of negative catalysis is very common in oxidation reactions. LUTHER's view which emphasises that negative catalysis cannot take place in a reaction which is entirely free from positive catalysts, is not substantiated by experimental evidence.

e. The organic substances act as negative catalysts by diminishing the concentration of the sulphite ion, which is the active agent in this oxidation; the diminution in concentration of sulphite ion is caused by the formation of a stable complex of the sulfite and the organic substance; this complex is not oxidized as readily as the sulphite ion.

c. Catalytic activity of the undissociated acid.

In recent years the question of acid catalysis has entered into a new period; and as a result of the accumulation of new observations and of increased exactitude in the measurement of the velocity of reactions, evidence has been obtained in support of the view that the catalysing power of an acid is not entirely due to the hydrogen ion, but that the undissociated acid also contributes to the observed effect.

This investigation had for its object the determination of the function of the undissociated parts of oxalic and picric acids in the hydrolysis of methyl acetate.

The experiments were all conducted at 45°. Dry pure potassium oxalate and sodium picrate were added in different quantities to diminish the ionisation of the respective acids. The former salt was crystallised from MERCK's pure sample, and the latter was prepared from pure materials and purified by repeated crystallisations.

The following summary of results is obtained [1])

Oxalic acid.

Conc. of acid.	Conc. of $K_2C_2O_4$	$\frac{\text{Acid Conc.}}{\text{Salt. Conc.}}$	K_1
·05 N	—	—	0·00091
"	·0038 N	13·16	0·00065
"	·0114 N	4·38	0·00044
"	·0174 N	2·37	0·00042
"	·0278 N	1·79	0·00038
"	·0590 N	1·02	0·00011

[1]) The experiments described here were finished in 1913.

Picric acid.

Conc. of acid.	Conc. of Sodium picrate.	Acid Conc. / Salt. Conc.	K_1
·03 N	—	—	0·00135
„	0·0031 N	9·67	0·00139
„	0·0050 N	6.00	0.00141
„	0·0513 N	0·58	0·00173
„	0·0778 N	0·38	0·00160
„	0·1161 N	0·25	0·00153
„	0·1597 N	0·18	0.00134
„	0·3066 N	0·09	0·00122

It will be evident from the foregoing tables that the velocity coefficients do not decrease proportionally with the decrease in the concentration of the hydrogen ions. In the case of oxalic acid the velocity coefficients fall off with the concentration of potassium oxalate; whilst in the case of picric acid the addition of sodium picrate produces at first an increase in the velocity coefficient and then when the concentration of sodium picrate reaches the value of 0·159 N, the velocity coefficients begin to fall off. This is explicable on the assumption that even undissociated acids are catalytically active in the hydrolysis of esters. But in view of the work of WALDEN (Jour. Amer. Chem. Soc. 1912, **35**, 1649) on the measurement of the di-electric constants of solutions, a different interpretation of these results is possible. WALDEN has shown with non-aqueous solutions that the di-electric constant and the ionising power of a solvent are enormously increased when electrolyts are dissolved in it. Naturally the degree of ionisation of the dissolved acid and along with it the concentration of hydrogen ions are also increased. Thus by the addition of salts of the same acids, there are two effects:

1. The diminution of hydrogen ions due to the increase of the common negative ion.

2. The increase in the concentration of the hydrogen ions due to the greater ionisation of the acid caused by the increase in the di-electric constant of the solvent.

It is evident that these two effects counteract each other.

In the case of potassium oxalate the first effect preponderates over the second and hence the velocity coefficient falls off with the concentration of potassium oxalate, whilst in the case of picric acid

the second effect predominates over the first and the velocity coefficient instead of decreasing, increases with the concentration of sodium picrate.

Moreover WALDEN has shown that there are two types of salts with regard to their effects on the di-electric constant of the solvent. He has observed that $N(CH_3)_4Cl$ markedly increases the di-electric constant of the solvent, whilst CH_3NH_2HCl affects this constant to a very slight extent. It is quite possible that even in aqueous solution salts like potassium oxalate, sodium acetate, etc. do not increase appreciably the ionising power of the solvent and the velocity of the reaction in its presence does not increase. In this way we can explain the negative effect of potassium oxalate and positive effect of sodium picrate on ester hydrolysis from the point of view of the change of the di-electric constant of the solvent due to the dissolution of electrolytes.

SUMMARY.

a. The hydrolysis of methyl acetate was investigated in presence of oxalic acid and picric acid and sodium picrate. In the former case, the velocity coefficient falls off, whilst in the case of picric acid, the velocity coefficient increases with the concentration of sodium picrate up to a certain extent and then decreases with the increase of the concentration of sodium picrate.

b. An explanation of these results is suggested on the basis of the increase of the di-electric constant and ionising power of the solvent observed by WALDEN when salts are dissolved in it.

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Chemistry. — *"Catalysis. IX. Thermal and photochemical reactions"*. By NIL RATAN DHAR. (Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of September 25, 1920).

In a foregoing paper (DHAR, Trans. Chem. Soc. 1917 **111**, 707) it was shown that the temperature coefficient of the oxidation of potassium oxalate by iodine has the value 7.2 for a 10° rise in the dark and this reaction is extremely sensitive to light.

It occurred to me that all reactions which have high temperature coefficients should be sensitive to light.

I have shown previously that most uni-molecular reactions have high temperature coefficients and I investigated the effect of tropical sunlight on several of these reactions, and the following results were obtained.

Ammonium nitrite decomposes fairly readily at about 33° in sunlight, whilst at 33° in the dark there is hardly any decomposition. The temperature coefficient for a 10° rise in the dark is about 4.5 (ARNDT, Zeit. Phys. Chem. 1901, **39**, 64).

The intramolecular transformation of acetyl chloranilide to para-chloracetanilide has the temperature coefficient 3.2 in the dark. (RIVETT, Zeit. Phys. Chem. 1913, **82**, 201) and BLANKSMA (Rec. trav. Pays. 1903, **22**, 290) has shown that the change is sensitive to light.

Similarly the pseudo-unimolecular reactions, the hydrolysis of cane sugar and the decomposition of potassium persulphate, are highly influenced by light. An aqueous solution of cane sugar when exposed for several days to tropical sunlight, becomes converted into the invert sugars.

GREEN and MASSON (Trans. Chem. Soc. 1910, **97**, 2083) have shown that potassium persulphate is slowly decomposed by water according to the following equation

$$K_2 S_2 O_8 + H_2 O = 2 K H S O_4 + O.$$

This reaction has the temperature coefficient 5 in the dark. I found that the reaction is very sensitive to light and the oxygen given off in 24 hours in sunlight is practically equal to that produced in about 15 days in the dark at 27°.

The decompositions of the sulfine bases and the tetraammonium compounds studied by VON HALBAN have high temperature coefficients

and these reactions when investigated would show great sensitiveness to light (Zeit. Phys. Chem. 1909, **67**, 129).

Cain and Nicoll (Jour. Chem. Soc. 1903, **83**, 470) have proved that the decomposition of the diazo salts has the value of about 5 for their temperature coefficients and it is well known that diazo salts are sensitive to light.

Pendlebury and Seward (Proc. Roy. Soc. 1889, **95**, 396) have shown that the reaction between $KClO_3$, KI and HCl has the temperature coefficient of about 4 in the dark and I have found that the reaction is very sensitive to light.

I have already shown (Trans. Chem. Soc. 1917, **111**, 707) that the oxidations of sodium formate by mercuric chloride and by iodine has 4.05 for their temperature coefficient. These two reactions are also very sensitive to light (Dhar, Proc. Akad. Wet. Amsterdam 1916, **24**, 1324).

I have shown that light markedly accelerates the reaction between iodine and oxalates and now I have tried to find out which part of the spectrum is active in this reaction. For this I exposed five small tubes containing a mixture of potassium oxalate and iodine in a spectrum obtained from a carbon arc-light. It was found that the iodine disappeared first in the tube held in the indigo portion near the violet end of the spectrum. Then that of the tube held in the blue region. The chemical change took place almost simultaneously in the tubes held in the green and violet portions of the spectrum and the colour of the tube in the red end was the last to disappear.

A mixture of mercuric chloride and potassium oxalate undergoes the following change in sunlight:

$$2HgCl_2 + K_2C_2O_4 = 2KCl + 2CO_2 + 2HgCl.$$

This decomposition can also be induced by lights obtained from a carbon arc, quartz mercury vapour lamp, and an arc obtained by passing alternating current in electrodes made of thorium and zirconium oxides. I have repeatedly observed that in tropical sunlight, a solution of ammonium cupric oxalate decomposes readily in glass vessels with the separation of metallic copper and evolution of carbon dioxide; but it was found impossible to bring forth this change by light obtained from the carbon arc or the thorium and zirconium oxides arc.

I have found that uranium nitrate markedly accelerates the photochemical decomposition of a mixture of mercuric chloride and potassium oxalate, but chromates having the same yellow colour as the

uranium salt exert a markedly negative effect. Mathews and Weeks (Journ. Amer. Chem. Soc. 1917, **39**, 635) have shown that uranium nitrate is also a positive catalyst in the photochemical oxidation of sodium sulphite. Moreover, it is wellknown that uranium salts markedly help the photochemical decomposition of organic acids (e.g.), oxalic, formic, lactic etc. Hence it appears that a uranium salt is a positive catalyst of great generality in photochemical reactions.

I have observed that manganese sulphate exerts a negative effect in the photochemical decomposition of a mixture of mercuric chloride and potassium oxalate. It has already been shown that manganese salts act as a negative catalyst in the reactions between phosphorous and chromic acids, formic and chromic acids, mercuric chloride and sodium formate, iodine and sodium formate, silver nitrate and sodium formate, silver nitrate and ferrousammonium sulphate, etc. So it seems that a manganese salt is a negative catalyst for light and dark reactions alike.

I have also observed the effects of the different parts of the spectrum on several other photochemical reactions by passing ordinary sunlight through different solutions and exposing the reacting substances to the filtered lights thus obtained and the results obtained are summarised below:

(1) $HgCl_2 + (NH_4)_2 C_2O_4 \rightarrow$	Blue, violet and ultra-violet more active than the red and infra-red.
(2) $I_2 + (NH_4)_2 C_2O_4 \rightarrow$	
(3) $FeCl_3 + (NH_4)_2 C_2O_4 \rightarrow$	
(4) Pyrogallol and Pyrogallate $+ O_2 \rightarrow$	practically uniform acceleration in different parts
(5) Hydroquinone $+ O_2 \rightarrow$	
(6) Cu_2Cl_2 (ammoniacal or acid) $+ O_2 \rightarrow$	
(7) Decomposition of $H_2S \rightarrow$	
(8) Quinine acid sulphate + $H_2Cr_2O_7 \rightarrow$	Blue and violet slightly more active than the red.
(9) $KMnO_4 + H_2C_2O_4 \rightarrow$	Violet and ultra-violet more active than red.

In a remarkable article Perrin (Annales de Physique 1919, t. XI, 1) has enunciated the following hypothesis:

"All chemical reactions are provoked by light radiations. Their velocities are determined by the intensity of the light radiations and depend on temperature to such an extent as the light intensity depends on temperature". By applying the idea of the emissive power of perfectly black bodies and its relation to temperature,

PERRIN has deduced the following equation connecting the velocity coefficient and the temperature:

$2 . 3\, d\, log_{10}\, k = \varrho v \frac{dT}{T^2}$, where $k =$ velocity coefficient, $v =$ wavelength of the activating radiation and $T =$ absolute temperature. From his calculations, it is seen that the wavelengths which are active in bringing forth the ordinary chemical changes vary from 2.56 to 0.8 microns. It is also seen that a reaction which is highly sensitive to the influence of temperature, has a small value for its activating wavelength, that is, a reaction of this type would be most sensitive to violet and ultraviolet end of the spectrum. From PERRIN's calculations it is seen that the reaction between $K_2C_2O_4$ and I_2, which has the high temperature coefficient of 7.2 in the dark, has 0.8 micron for the wavelength of its activating radiation. In other words, this reaction would be most sensitive to light near the red end of the spectrum. But it is experimentally shown that this reaction is not sensitive to the indigo part near the violet end of the spectrum. My own experiments on several photochemical reactions have shown that the blue and violet portions of the spectrum are most active so far as chemical effects are concerned. Although the hypothesis of PERRIN is still of a qualitative nature, it is a highly suggestive one and my experiments give this hypothesis a sort of general support.

I have tried to prove experimentally that reactions, which are most sensitive to the influence of temperature, are also most sensitive to the influence of light. In a foregoing paper, I have advanced the hypothesis that temperature and light affect a chemical change in a similar way. The experimental evidence brought forward in this article, as well as PERRIN's hypothesis that all chemical changes are induced by radiations, give additional confirmation to my hypothesis regarding the identity of effects of temperature and light on chemical reactions.

Summary:

a. Evidence has been brought forward in support of the view that reactions, having large temperature coefficients, are sensitive to light. Hence for a chemical reaction, sensitiveness to the influence of temperature and sensitiveness to light radiations go hand in hand.

b. The indigo part near the violet end of the spectrum is most active in the reaction between $K_2C_2O_4$ and I_2; blue and violet parts more active than the red in the following cases:

$(NH_4)_2C_2O_4 + HgCl_2$, $(NH_4)_2C_2O_4 + FeCl_3$, $H_2C_2O_4 + KMnO_4$ and Quinine bisulphate + $H_2Cr_2O_7$.

c. Uranium salts are general positive catalysts in photochemical reactions, whilst manganese salts are general negative catalysts in light and dark reactions alike.

d. PERRIN's hypothesis that all chemical reactions are induced by radiations support the view that the effects of temperature and of light on chemical reactions are of an identical nature.

e. A solution of ammonium cupric oxalate decomposes with the separation of metallic copper and evolution of CO_2 in tropical sunlight, but not in carbon-arc-light or the zirconium + thorium oxides-arc-light.

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Chemistry. — "*Catalysis.* **X.** *Explanation of some abnormally large and small temperature coefficients*". By NIL RATAN DHAR. (Communicated by Prof. ERNST COHEN).

(Communicated at the meeting of September 25, 1920).

SKRABAL (Monatsh. 1914, **35**, 1157) has shown that the velocity of formation of iodate from iodine and iodide in a mixture of sodium carbonate and sodium bicarbonate solutions has $\frac{k_{t+10}}{k_t} = 45$. When a similar reaction was effected in sodium acetate solution, the temperature coefficient is 2.

The velocity of decomposition of iodate in a mixture of acetic acid and sodium acetate solution has $\frac{k_{t+10}}{k_t} = 1.34$. The same reaction in a mixture of disodium and monosodium phosphates gives a temperature coefficient 1.26; in a mixture of KF and HF, the temperature coefficient has the value 0.9 to 1.04 and a mixture of sodium sulphate and sodium hydrogen sulphate leads to the value of 0.85.

SKRABAL remarks that the temperature coefficient must necessarily undergo a change when the substances, which affect the time equation, are transformed into complexes. The relationship between the temperature coefficient T of the original reaction and T′, that of the reaction between the complex substances is governed by the formula,

$$T'/T = e^{10/RT\,(T+10)\,(mQ_1 + nQ_2 + \ldots\ldots + xq_1 + yq_2 + \ldots\ldots)}$$

in which Q and q represent the heat changes of the complex reaction and the sum $(m + n + \ldots\ldots + x + y + \ldots\ldots)$ indicates the order of the reaction. This formula indicates that a great variability of T is to be expected from reactions of the higher orders.

In a foregoing paper (Annales de Chimie et de physique 1919, t. XI, 130) I have definitely proved that this conclusion of SKRABAL, which states that the temperature coefficients of polymolecular reactions are, in general, greater than those of unimolecular ones, is not supported by experimental evidence.

SKRABAL investigated these two polymolecular reactions:

$$3\,I_2 + 6\,OH' = 5\,I' + I\,O'_3 + 3\,H_2O \text{ and}$$
$$I\,O'_3 + 5\,I' + 6\,H = 3\,I_2 + 3\,H_2O.$$

He has shown that the second reaction has a temperature coefficient less than unity (about 0.83) in presence of sodium sulphate and sodium bisulphate (Zeit. Elektrochem. 1915, **21**, 461).

As these results are rather peculiar, it was thought worth while to re-investigate some of these cases.

A dilute solution of iodic acid was prepared and potassium iodide added to this solution. The reaction is very rapid and it is practically impossible to determine its temperature coefficient; when the two solutions are mixed at 0°, iodine immediately separates. The mixture is divided into two parts, one of the two tubes is put into ice and the other heated to boiling. Now the hot tube is cooled and brought to the same temperature as the other and the colour of the two tubes compared. Generally it is very difficult to find any difference in the two tubes. Sometimes the heated seems more pale probably due to the volatilisation of iodine when the tube is heated. Consequently the temperature coefficient without any sulphate is practically unity.

Similar experiments were made in presence of concentrated solutions of sodium sulphate and magnesium sulphate. In presence of these sulphates, a mixture of iodic acid and potassium iodide liberates slightly less iodine at a high temperature than at ordinary temperatures, hence a slight negative effect, of increase of temperature on the velocity of the reaction between iodic acid and potassium iodide, is observed.

On the other hand, potassium sulphate, potash alum, manganese sulphate etc. are quite ineffective in changing the temperature coefficient of the reaction between iodic acid and potassium iodide. The behaviour of potassium sulphate is different from that of sodium sulphate, since a saturated solution of sodium sulphate is richer in SO_4'' ions than a saturated solution of potassium sulphate at the same temperature. The temperature coefficient of the reaction between iodic acid and potassium iodide in presence of the above sulphates is practically unity.

Ammonium and zinc sulphates behave differently and in their presence the temperature coefficient becomes greater than unity. Marked difference is noticeable in the two tubes; the tube, which is heated, contains much more free iodine than the tube kept at 0°.

The explanation of this behaviour is connected with the phenomenon of hydrolysis. The sulphates of sodium, magnesium etc. are very slightly alkaline, since the basic portions in these salts are stronger than the acid portion. At higher temperatures more OH'-ions are produced, since temperature greatly increases the amount

of hydrolysis, and these OH'-ions react on the iodine which is set free re-forming iodide and iodate.

Hence at the higher temperatures, less iodine seems to be formed from the mixture of iodic acid and potassium iodide in presence of concentrated sodium or magnesium sulphate.

On the other hand, solutions of zinc and ammonium sulphates produce $H^{\cdot}$-ions due to hydrolysis and these $H^{\cdot}$-ions are very active in liberating iodine according to the following equation:

$$I O'_3 + 5 I' + 6 H = 3 I_2 + 3 H_2O.$$

Moreover, I have repeatedly observed that addition of acids produces more iodine, from a mixture of iodic acid and potassium iodide, than in the absence of acids.

Hence the abnormal effect of temperature on the velocity of the reaction between iodic acid and potassium iodide in presence of sodium sulphate ascribed by SKRABAL to complex formation, is really due to secondary changes produced by the interaction of the products of the hydrolysis on the reacting substances.

A similar explanation is applicable to the small temperature coefficients obtained in the reaction between iodic acid and potassium iodide in presence of sodium acetate, sodium phosphate and potassium fluoride; because all these salts are alkaline due to hydrolysis.

The reaction between iodic acid and potassium iodide is extremely rapid even at 0°. The reactions between KI and $K_2S_2O_8$ and KI and H_2O_2 have smaller velocities than that between HIO_3 and KI. These two reactions have temperature coefficients greater than unity. Experiments were made on the effect of concentrated $MgSO_4$ solution on the influence of temperature on the reactions between HI and $K_2S_2O_8$ and HI and H_2O_2. Even in presence of $MgSO_4$, these two reactions have temperature coefficients greater than unity. The hot tubes contain much more iodine than the cold ones.

In this connection, it is interesting to observe that the solubility of iodine in KI or HI is greatly diminished by the presence of $MgSO_4$.

HCl does not produce an increase in the amount of iodine liberated in the following cases:

(*a*) $K_2S_2O_8$ + KI, (*b*) $K_2S_2O_8$ + HI, (*c*) Ferric nitrate + KI.

In the following cases, HCl markedly increases the amount of iodine

(*a*) H_2O_2 + KI, (*b*) H_2O_2 + HI, (*c*) HIO_3 + KI, (*d*) HIO_3 + HI,
(*e*) $H_2Cr_2O_7$ + HI, (*f*) $K_3Fe(CN)_6$ + KI, (*g*) HNO_2 + KI.

The last two reactions have temperature coefficients greater than unity even in presence of HCl.

The displacement of iodine even in very dilute solutions of KI by chlorine or by bromine is very rapid and almost instantaneous even at 0°. The temperature coefficient is practically unity.

The liberation of iodine from KI,$KMnO_4$ and H_2SO_4 is almost instantaneous even at 0°. The temperature coefficient is practically unity.

The liberation of iodine from KI + $KClO_3$ and H_2SO_4 or HCl, KI + KBrO + H_2SO_4 or HCl has a measurable velocity and temperature has a marked influence on these reactions, but KIO_3 + KI + HCl or H_2SO_4 liberates iodine at once and no effect of temperature could be detected.

The reactions between iodine and sodium thiosulphate, and iodine and sulphite are extremely rapid even at 0°. There is hardly any possibility of measuring the velocity of the reactions concerned.

In a foregoing paper (Jour. Chem. Soc. 1917, **111**, 707) I have shown that the oxidation of oxalic acid by chromic acid has the temperature coefficient 1.95, but in presence of Na_2SO_4, $MgSO_4$ and NaF, the temperature coefficient goes down to 1.63, 1.61 and 1.59 respectively. The explanation seems to me to be the same as in the Skrabal reactions. The reaction between oxalic acid and chromic acid is accelerated by $H^{\cdot}$ ions. Sodium sulphate, sodium fluoride etc. are hydrolysed to a much greater extent at a higher temperature than at the ordinary temperature and the OH' ions produced at the high temperature neutralize the $H^{\cdot}$ ions existing in the solution and hence the actual velocity of the reaction does not rise so high as it should have been if there were no increased hydrolysis and consequent generation of OH' ions at these temperatures. In other words, the effect of temperature is partly neutralized.

Exactly similar results were obtained by Harcourt and Esson (Phil. Trans. **186** A, 1895, 817) in the reaction between HI and H_2O_2. They obtained the value 1.4 for the temperature coefficient of the above reaction in presence of $NaHCO_3$, whilst in presence of HCl, H_2SO_4 etc., the temperature coefficient is 2.1; Harcourt and Esson could not account for this discrepancy. The explanation is the same as that of the Skrabal reaction. Sodium bicarbonate is alkaline in aquoeus solution and it produces OH' ions in a greater quantity at higher temperatures than at ordinary temperatures and these OH' ions react on the iodine which is produced, forming iodide and iodate. Hence at the higher temperatures less iodine seems to be formed. In other words, the effect of temperature is partly neutralized and we get the small value (1.4) for the temperature coefficient of the reaction between HI and H_2O_2 in presence of $NaHCO_3$.

On the other hand, SKRABAL got the value 45 for the temperature coefficient of the reaction $3I_2 + 6OH' = 5I' + IO'_3 + 3H_2O$, in presence of sodium carbonate and bicarbonate. Here the hydrolysis of the salts produce OH' ions which are active in the change and helps the effect of temperature. The increase of temperature increases the hydrolysis and hence the OH' ions are also increased and the velocity of the reaction is increased due to this effect in addition to the usual effect of temperature increasing the velocity of the reaction. In other words, the effect of temperature is intensified.

Hence the abnormally large effect of temperature is explained.

Summary:

a. A dilute solution of iodic acid and potassium iodide react very rapidly even at 0°. The temperature coefficient cannot be exactly determined and is probably equal to unity.

b. In presence of sodium and magnesium sulphates slightly less iodine is liberated from iodic acid and potassium iodide at higher than at lower temperatures. The explanation is that at higher temperatures more OH' ions are produced due to increased hydrolysis of sodium or magnesium sulphate and these OH' ions react on the iodine which is forming and thus regenerate iodide and iodate. Hence in presence of Na_2SO_4, the temperature effect is partly counter-acted.

c. Manganese sulphate, potassium sulphate, alum etc. have no action, whilst in presence of ammonium and zinc sulphates, the temperature coefficient of the reaction between iodic acid and potassium iodide becomes greater than unity. Solutions of zinc and ammonium sulphates produce more $H^{\cdot}$ ions at higher temperatures and these ions are very active in liberating iodine from iodic acid and potassium iodide.

d. A similar explanation is applicable to the small temperature coefficients obtained in the reactions between 1. iodic acid and potassium iodide in presence of sodium acetate, sodium phosphate, potassium fluoride etc., 2. chromic acid and oxalic acid in presence of sodium sulphate, magnesium sulphate, sodium fluoride etc., 3. hydrogen peroxide and hydrogen iodide in presence of sodium bicarbonate.

e. Abnormally large values of temperature coefficient for the reaction $3I_2 + 6OH' = 5I' + IO'_3 + 3H_2O$, in presence of Na_2CO_3 and $NaHCO_3$, are also due to hydrolysis of the carbonates.

f. The following reactions have measurable velocities and their

temperature coefficients are greater than unity even in presence of $MgSO_4$ or HCl:

(1) $KI + K_2S_2O_8$, (2) $KI + K_3Fe(CN)_6$, (3) $KI + HNO_2$.

On the other hand, the following reactions are almost instantaneous even at 0° and their temperature coefficients are about unity:

(1) $KI + H_2SO_4 + KMnO_4$ (2) $KI + Br$, (3) $KI + Cl$.

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Physiology. — *"On Fibrillation of the Heart"*. (First part). By Dr. S. DE BOER. (Communicated by Prof. I. K. A. WERTHEIM SALOMONSON).

(Communicated at the meeting of March 27, 1920).

I.

It had struck me as early as 1914 that a single induction-shock applied to the ventricle repeatedly engenders fibrillation of this chamber of the heart. I did not study this phenomenon any further, since at that time I was studying the electrograms of the extra-systoles and of the postcompensatory systoles.

When, however, I continued my alternation-experiments with the bled frog's heart through extra-stimulation, I noticed the above phenomenon so frequently that I felt called upon to study the relations, under which this fibrillation took place, more closely. It now appeared that fibrillation of the ventricle occurred after a single induction shock only when this was applied directly after the close of the refractory stage which always accompanies the systole immediately preceding. This is clearly illustrated by the curves of fig. 1, which were registered [1]) half an hour after the bleeding of a suspended frog's heart. In the upper row of curves an induction shock was given to the base of the ventricle at 1 a short time after the close of the refractory stage.

Fibrillation of the ventricle was the result which manifested itself in the string-curve by totally differing deflections, whose tempo was very irregular. Similar results were achieved at 2, 6, and 8.

We notice that the post-undulatory pause, after fibrillation excited in 6, may also be lacking (after 2). After 3 an extra systole is interpolated by the extra-stimulus, a phenomenon that may occur with a slow heart-beat, as has been first shown by TRENDELENBURG. In this case the stimulus was administered at a much later period of the ventricle (towards the close of the T-deflection), so that a fully co-ordinated extra-systole was the result. In the same way a complete extrasystole is generated at 7, because here also the stimulus

[1]) In this and the following registrations a non-polarizable electrode was placed on the auricles and one on the apex of the ventricle. The tension of the string was in all experiments such that 1 mV. yielded a deflection of $1^1/_2$ mm.

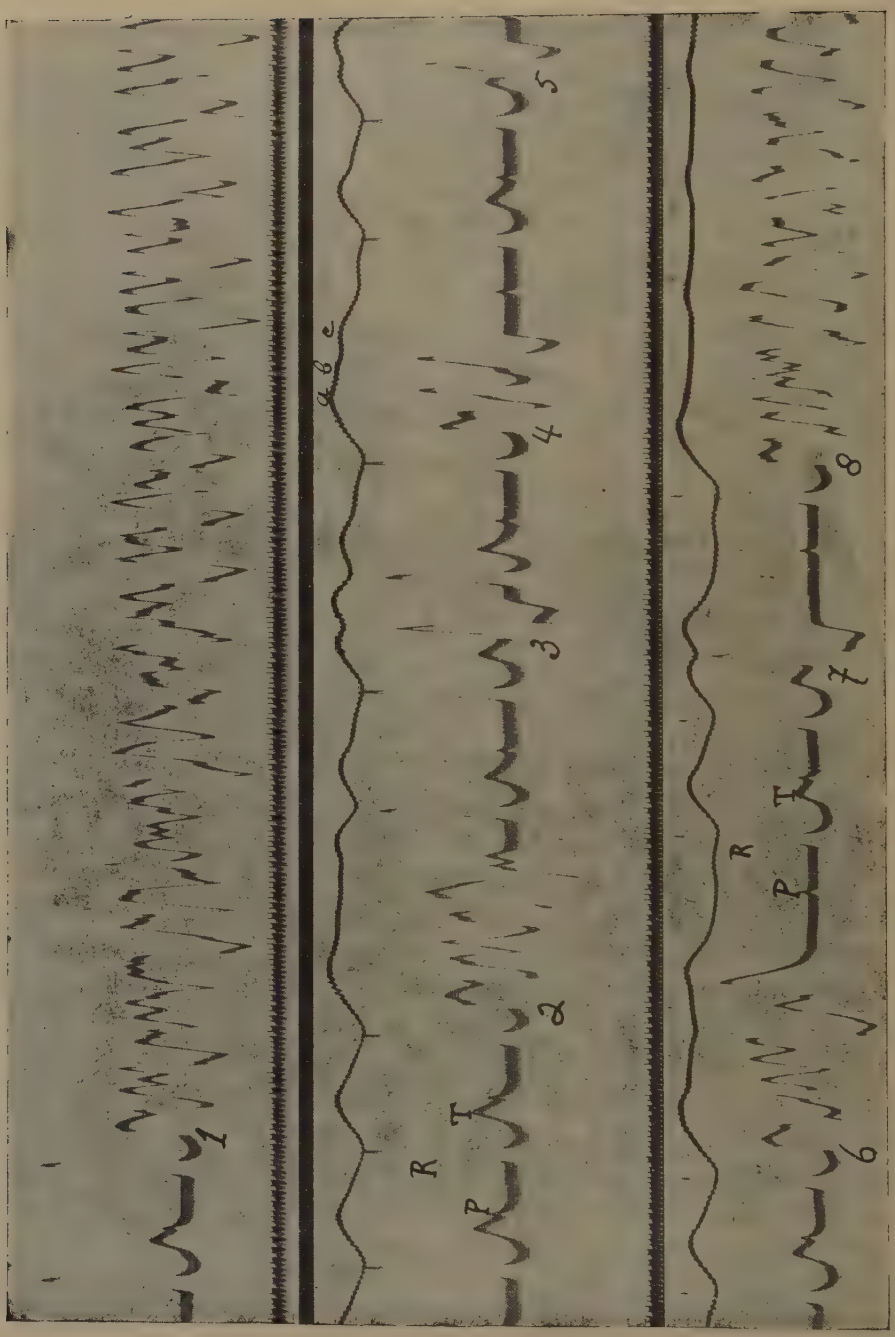

Fig. 1.

was applied later. Not a single exception to this did I find in a large number of experiments with more than 100 frogs.

While fibrillation of the ventricle could be generated only by one induction-shock at the very commencement of the excitable period, I invariably obtained a fully co-ordinated extrasystole, when the stimulus was applied at a later stage of the excitable period with the same force and at the same spot.

To the brief delirium, originating at 4 after the extra-stimulus I shall revert lower down.

Fig. 2 shows that during an experiment the metabolic condition of the ventricular muscle must deteriorate considerably before delirium can be brought about. In the upper row a stimulus was twice administered to the base of the ventricle 15 minutes after the bleeding (at 1 in the beginning, at 2 in the middle of the descending branch of the *T*-deflection). In both cases a complete extra-systole of the ventricle appeared. The second row of curves was registered a quarter of an hour after the bleeding and now at 3 a little before the middle of the descending branch of the *T*-deflection an extra stimulus is given to the base of the ventricle. Although the stimulus was now applied later than at 1, ventricular fibrillation now follows. Now that the general condition of the ventricular muscle is grown worse in a quarter of an hour, the stimulus on the ventricle must be applied still later to generate an extra-systole. It is obvious that the electric deflections are again very irregular. Shortly after this registration this fibrillation stopped spontaneously. When a few minutes afterwards I applied again a stimulus to the ventricle, a permanent fibrillation of the ventricle ensued, which I registered for 1½ hours (see Fig. 3). I regret that the commencement of the fibrillation was not registered. The top curves were photographed 5 minutes after the beginning of the delirium. We see that now the deflections, as in fig. 2, are irregular. The 2nd row was registered ¾ hour after the commencement of the fibrillation. Now the curves present a totally different aspect. A certain regularity in the deflections can be observed. Every time three smaller deflections occur between two larger ones, but each of four successive deflections is different from the others and the tempo is irregular. But these groups of 4 deflections recur continually. The bottom curves were taken 1½ hours after the commencement of the fibrillation. Though the deflections are slightly altered the regularity of the delirium remains. In both registrations the two successive, equal deflections are at the same distance from each other. In the suspension-curves the regular deflections of the auricular contractions may be observed (in the

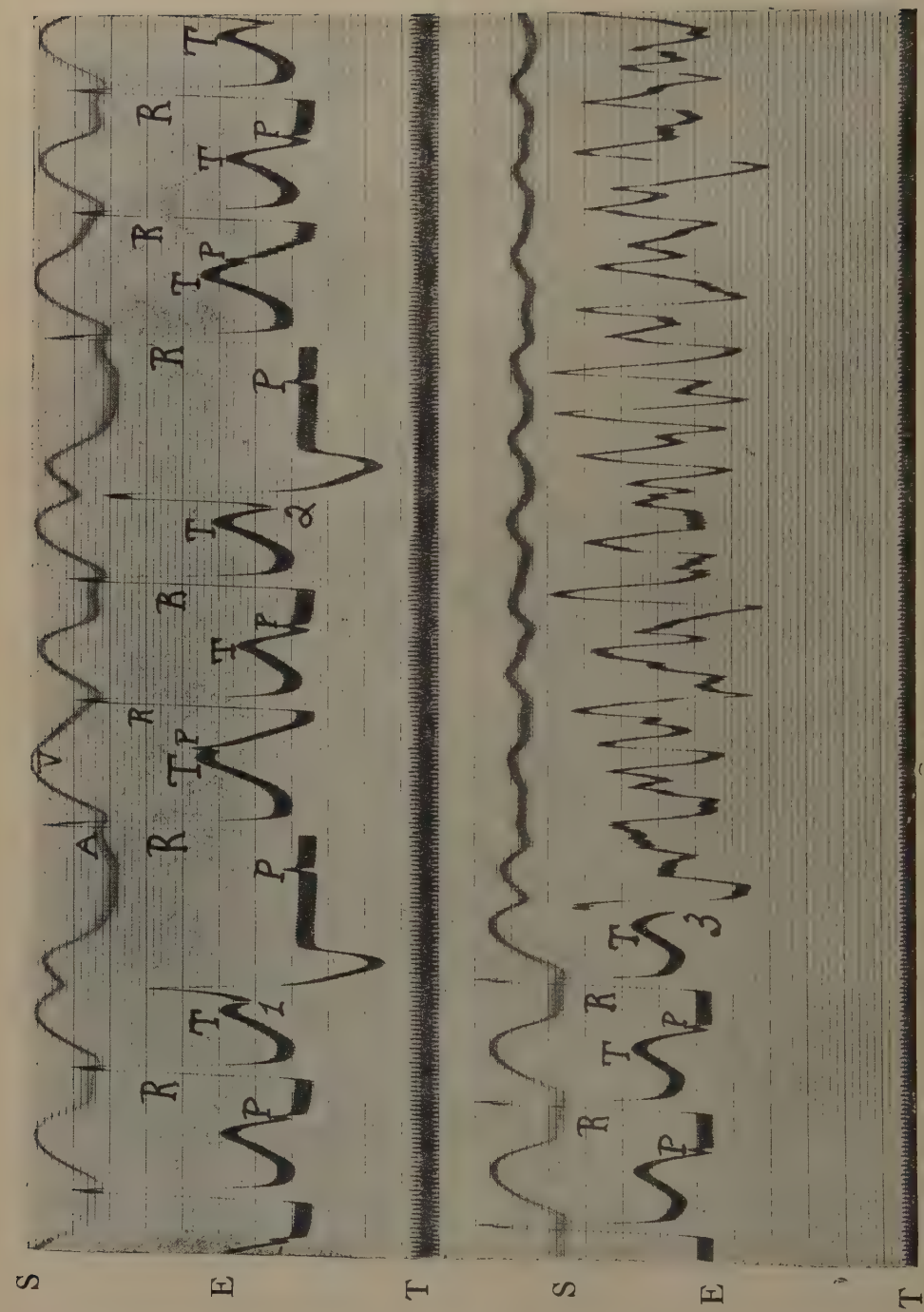

Fig. 2.

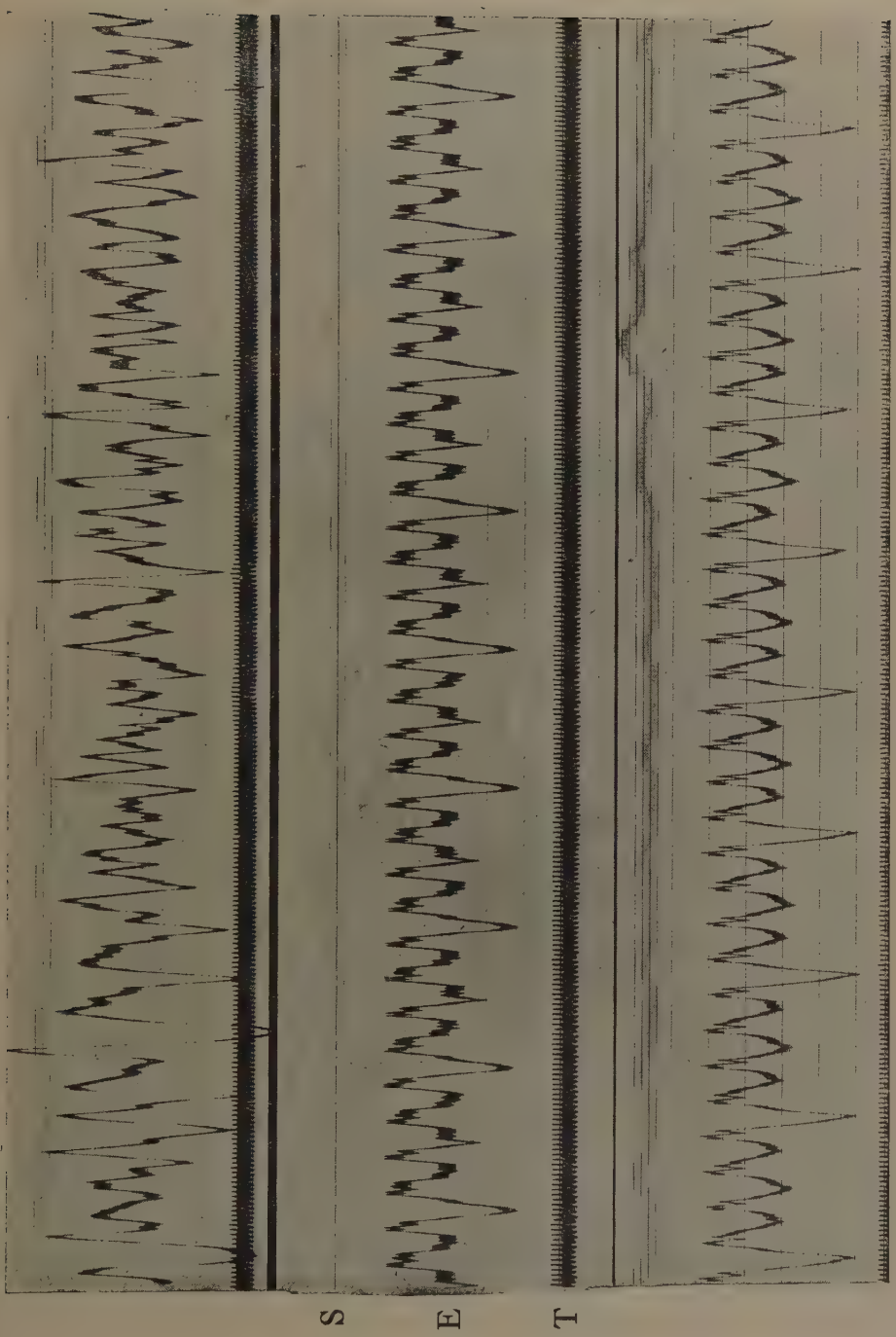

Fig 3.

lower registration the suspension-curve is slightly interfered with by a momentary movement of the frog). Also through inspection I noticed that the auricles continued beating during the fibrillation.

I also possess the registration of two more frog's hearts that kept fibrillating after a stimulus. Here also the deflections of the string were initially irregular and here also they became more regular afterwards. In these registrations large and small deflections were alternating and the auricles continued beating regularly.

Significance of the experimental results obtained for an explanation of ventricular fibrillation.

Before accounting for ventricular fibrillation in a way different from all previous interpretations, I will just summarize the main results of this investigation. It should be remembered that the ventricle can only be made to fibrillate by an extra-stimulus if this stimulus is applied directly after the close of the refractory stage. Fibrillation never appears when the stimulus is given later with the same force and at the same spot; if it is, it will result in an ordinary extrasystole.

To these facts I attach great value. So the ventricle will begin to fibrillate after an extra-stimulus only when its metabolic condition is bad. This condition is still bad at the beginning of the excitable period, because in so short an interval after the termination of the preceding systole the ventricular muscle has not been able to recover itself. From this bad metabolic condition of the ventricle it follows:

1. That the contractility of the ventricular muscle is bad. After an extra-stimulus there is a brief small contraction. *This brief extra-contraction is accompanied by a brief refractory stage.*

2. That the conductivity of the excitation through the ventricle is slight.

These two circumstances are conclusive for the origin of the delirium. These conditions are quite different when the stimulus is applied at a later period. Then the metabolic condition is much better, because after the preceding systole the ventricle has had more time for recovery. Consequently the contractility and the conductivity are much better; then the excitation passes rapidly through the ventricle and a properly co-ordinated extra-systole results from the stimulus.

In order to fully understand the origin of the delirium, we must first consider the brief delirium, since in some of our experiments the delirium was only of very short duration and consisted of 2 or

3 deflections in the mechanogram and in the electrogram. This is instanced in Fig. 1 (2nd row of curves at 4). Here we see after the electric stimulus 3 small deflections in the suspension-curve (*a*, *b* and *c*) with which electric deflections correspond. Now what does this mean? When looking at 2 or 3 deflections, we observe a phenomenon formerly described by me as deformed ventricular systoles and which is known in the literature by the name of ventricular peristalsis. Similar deformed systoles also occur after digitalis poisoning[1]). We illustrate this by a series of curves registered from a frog's heart 25 minutes after a subcutaneous injection in the thigh of 14 drops of digitalis dialysate (Fig. 4). The first ventricular curve of the figure consists of two parts; first the suspension curve rises up to a certain point and at the beginning of the dilatation line a second rise begins. This form of the curve owes its origin to the circumstance that first a part of the ventricular muscle begins to contract; subsequently, owing to the bad metabolic condition the rest of the muscle comes into action with a prolonged latent stage; this causes a retarded contraction.

The electrogram registered at the same time fully confirms this statement. The third ventricular curve of the figure presents a break in the ascending branch and is, therefore, also deformed. During these deformed ventricular systoles the whole muscle is indeed made to contract, but in 2 or 3 tempos. The same is the case with the brief delirium. After the extra stimulus which affects the ventricle at a moment when the recovery of the muscle is still unsatisfactory, part of the ventricle begins to contract. The proceeding "Erregung" imparts contraction to the following portion only after a long lasting latent stage, so that the "Erregung" passes through the ventricle in two stages. The brief delirium, then, is nothing but a deformed fractionated extrasystole.

Now upon this basis we can readily conceive the origin of the longer fibrillation in our experiments. As set forth heretofore, the refractory stage of the contraction, generated at the outset of the excitable period, is shortened. This shortening is of great moment for the lengthening of the delirium. When the "Erregung", after an extra-stimulus, has gone through the ventricle in stages, the time of such a circulation is lengthened considerably. Now when the excitation wave reaches the starting point again, it begins to contract again, because the short refractory stage of the preceding contraction has already come to a close. Again the "Erregung" proceeds through

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[1]) Arch. Neêrl. de Physiologie. Tom. III, p. 69, 1918.

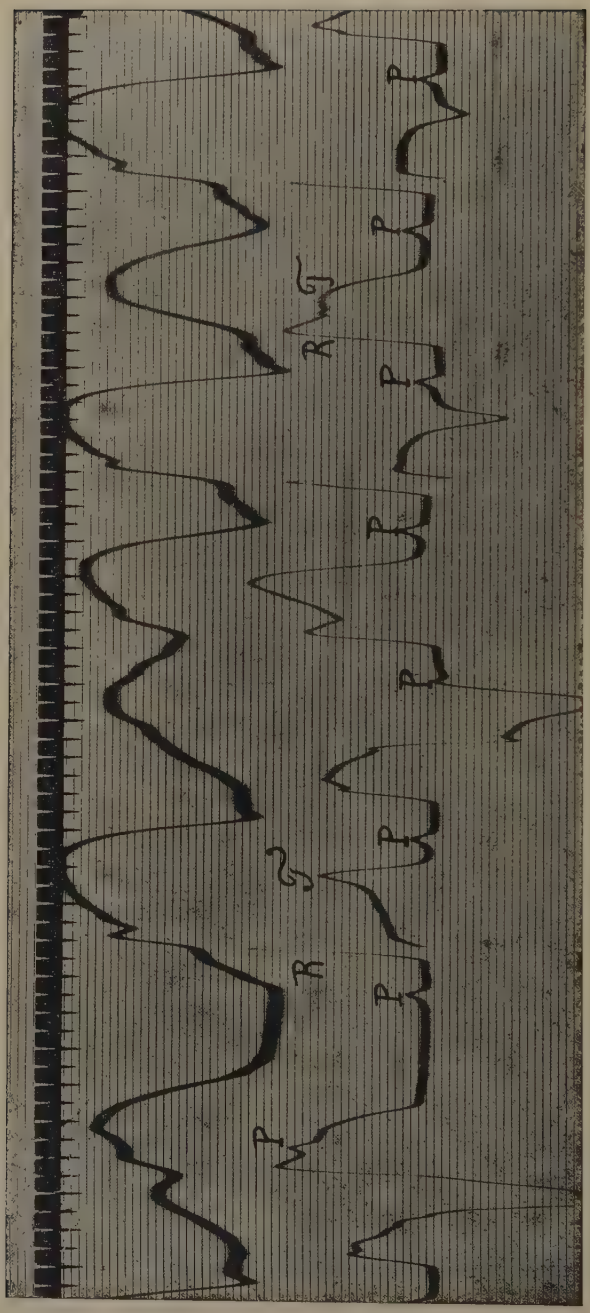

Fig. 4.

the ventricle and again by jerks. Thus the excitation wave keeps on circulating through the ventricle like an ignis fatuus, and fibrillation is checked only when it strikes on a refractory region. Then the post-undulatory pause sets in, which however may also be absent. (Fig. 1 after 2 in the second row).

After an extra-systole, elicited later in the excitable period, the excitation-wave does not begin a second course, because then it is checked by the refractory stage, which with this extra-systole is of longer duration. The same relations exist with the normal rhythmic systoles. If in this case the refractory stage were absent or much shorter, the excitation-wave would always continue its course in the closed muscular system of the ventricle, which would not be able to pulsate rhythmically under the influence of the sinus-impulses.

According to my theory, therefore, fibrillation of the heart is brought about by a non-coördinated contraction, not as WINTENBERG conceived this; viz. that sundry sources of contraction are functionating independently; according to my theory the various regions of a ventricle contract successively and an "Erregung" being once elicited may pass through a ventricle several times running; the ventricular delirium consists of a string of fractionated ventricular systoles. For fibrillation two conditions must be fulfilled *at the moment when it originates:*

1. The refractory stage must be shortened.

2. The conductivity of the stimulus through the ventricle must be insufficient. Both conditions are fulfilled in my experiments. Directly after the close of the refractory stage the metabolic condition of the ventricle is bad, contractility is slight, so the refractory stage, accompanying a contraction, is short; moreover the conductivity through the ventricle is insufficient.

WINTERBERG and ROTBERGER believed that the only essential condition for the origin of fibrillation was a much shortened refractionary stage. This is true if only conductivity is also bad. Only then will the phenomenon come forth.

Now the question arises, why after digitalis poisoning of the

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[1]) Incessant fibrillation may succeed when the "Erregung" after one circulation always arrives at the starting point again at a moment when the recovery is still insufficient. Thus the excitation-wave may be emprisoned in a ventricle and every time renew its course. Especially when (as in Fig. 3) the delirium becomes regular; then the chance of a spontaneous termination is little, as, when the excitation-wave has gone through the ventricle some times in succession in the same way, this may be repeated every time without the "Erregung" being checked by a refractory region.

frog's heart deformed ventricular systoles are generated, whereas it never brings about fibrillation of the ventricle. This finds an explanation in the fact that after digitalis poisoning (in a toxic dosis [1])) the refractory stage of the ventricle is lengthened instead of shortened. Conductivity is then bad, however, so that a single deformed ventricular systole can arise, but the "Erregung" cannot pass through the ventricle a second time.

[1]) When speaking of digitalis-poisoning in a toxic dosis, I mean a dosage that lengthens the refractory stage and retards conductivity.

Physiology. — "*On Fibrillation of the Heart.* (Part. II). *On the Relation between Fibrillation of the Heart and "Gehäufte" Extra-systoles*". By Dr. S. DE BOER. (Communicated by Prof. I. K. A. WERTHEIM SALOMONSON).

(Communicated at the meeting of March 27, 1920).

II.

It is remarkable that while clinicians already suspected a relation between fibrillation and "gehäufte" extra-systoles, both abnormal cardiac actions could be generated under precisely the same conditions in the frog's heart. Such was the case in some of our experiments when at the close of the refractory stage of the ventricle we observed a series of systoles of this chamber instead of fibrillation after the application of an induction shock.

This phenomenon is illustrated in the three figures which we will now describe:

In fig. 1 are shown the suspension curves and electrograms of a bled frog's heart [1]). At 1 on the summit of the negative *T*-deflection an induction shock is applied on the base of the ventricle. This evokes an extra-contraction of the ventricle, which is represented in the string-curve by a ventricular electrogram of which the *R*-deflection is broadened, and at the same time the magnitude of the negative *T*-deflection is increased. Previous investigations made by me went to show that a broadening of the *R*-deflection and a change of the *T*-deflection in a negative sense resulted from a slowing of the conduction of the excitation through the ventricle. In the experiment before us, the reason why after the administration of the induction shock the conduction of the excitation is slowed, is that the refractory stage of the preceding systole had come to a close a short time before. The metabolic condition of the ventricle was consequently still bad. A second result from this bad metabolic condition is the bad contractility of the ventricular muscle. The extra-systole revealing itself after the stimulus, is small (as may be read from the

[1]) In every figure the electrograms were taken by placing a non-polarizable electrode at the apex and one on the auricles. The tension of the string was such that the interpolation of 1 mV. caused a deflection of the string of $1^1/_2$ mm. Time was registered in $^1/_5$ seconds.

suspension-curve). It is accompanied by a brief refractory stage. During this extra-systole we have, then, on the one side a slackened conduction of the excitation through the ventricle and on the other a brief refractory stage.

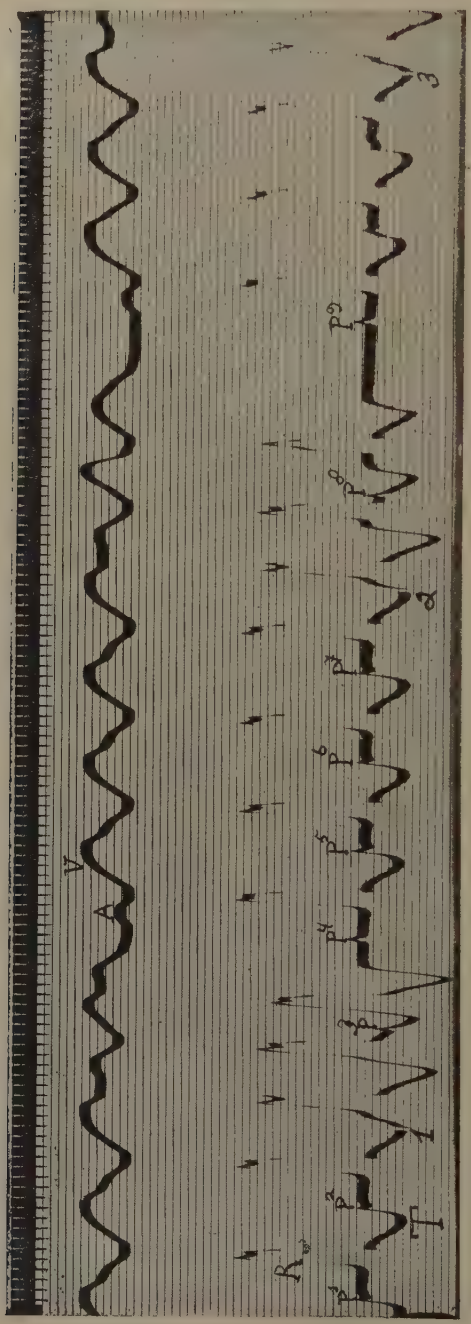

Fig. 1.

These two factors contribute to the origin of "gehäufte" extrasystoles. The excitation-wave, it is true, has not traversed the ventricle in stages, but the time required for a circuit, has nevertheless increased. The refractory stage being shortened, the excitation-wave performs again its circuit through the ventricle, because when it has arrived at the starting point, the ventricle has at that spot become excitable again after the shortened refractory stage. The second time the excitation-wave again traverses the ventricle slowly and again the contraction is of short duration. In this way the excitation-wave may move round the ventricle several times running and engender a series of reduced ventricular systoles.

The electrograms imaging this process show the indicated characteristics of a slackened conduction of the excitation-wave [1]). After the first extrastimulus three "gehäufte" extrasystoles revealed themselves. During these three extra-systoles we see in the electrogram-curve one P-deflection (P_3) preceding the next P by exactly one periodic interval. It would seem, then, that during these "gehäufte" systoles of the ventricle the periodicity is not disturbed. At 2 the stimulus is repeated on the apex of the negative T-deflection and again three "gehäufte" extrasystoles [2]) are generated. Now also the pulsations of the auricle are undisturbed.

The curves of Fig. 2 are derived from the same frog's heart. At 1 an induction shock was applied to the base of the ventricle towards the close of the T-deflection, which resulted in three "gehäufte" extra-systoles. At 2 the stimulus was renewed at the same time of the ventricular period, which produced a curve illustrating a mingling of irregular fibrillation and "gehäufte" extrasystoles. The first curve after the stimulus is a distinct extrasystole (as can be concluded from the deflections of the string, which show an R-deflection and an intense negative T-deflection). Subsequently the electric curve becomes very irregular and at the close two distinct extrasystoles appear again, each with an R- and T-deflection. When the ventricular base is stimulated again at 3, two extrasystoles are evolved.

Fig. 3 shows the curves of another frog's heart.

The electrograms of the normal rhythmic ventricular systoles

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[1]) The influence of the rate of conduction upon the form of the ventricular electrogram is discussed by me extensively in Pflüger's Arch. Bd. 173, Seite 78, 1918 and Arch. Néerl. de Physiologie, tome III (1918) p. 7.

[2]) It will be seen that the duration of the pause after the "gehäufte" extrasystoles is very different sometimes, as appears from the figures. The time of the post-undulatory pause may also be very different. I purpose to revert to these facts in a later communication.

exhibit broad *R*-deflections and large corresponding negative *T*-deflections. Here we discern — as is always distinctly the case with slow conduction of the excitation-wave — in each ventricular

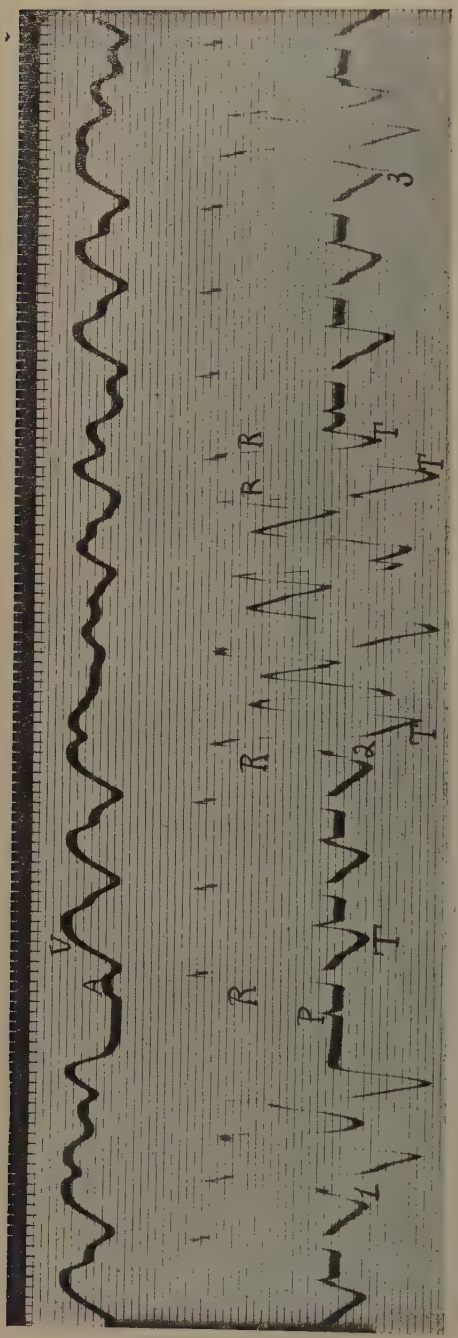

Fig. 2.

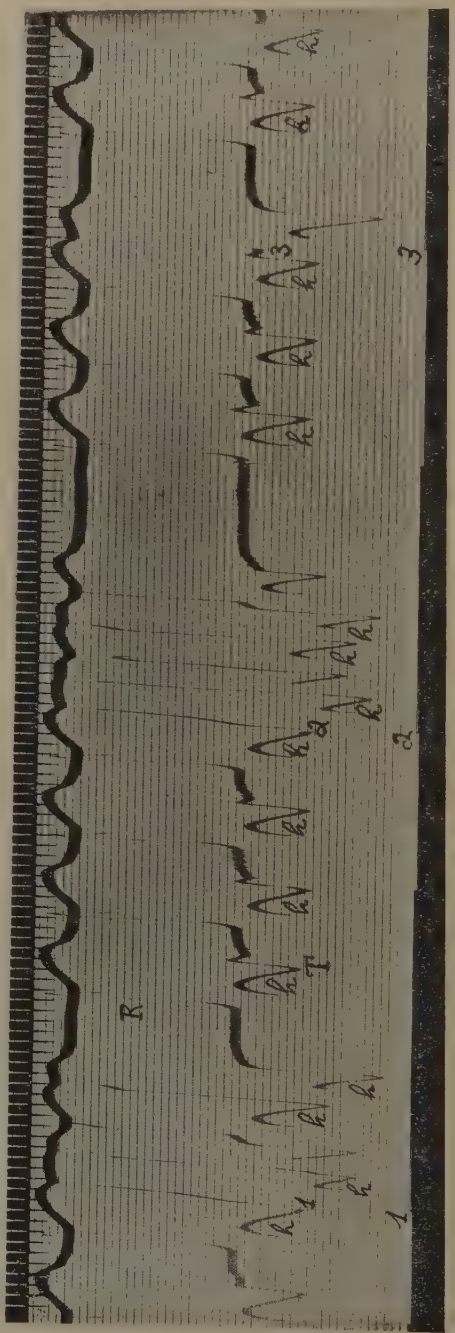

Fig. 3.

electrogram as a sign of persisting basal negativity the heel of SAMOJLOFF (marked by an *h* in the figure) cut into the retarded apical negativity.

At 1 the base of the ventricle receives an induction shock a little after the apex of the negative *T*-deflection. Four connected extra-systoles are evoked by it. From the accompanying ventricular electrograms it is evident that the conduction of the excitation wave through the ventricle is considerably slowed with each extrasystole. We infer this from the marked broadening of the *R*-deflections and the considerable change of the *T*-deflections in a negative sense. The heel of SAMOJLOFF is clearly observable in each electrogram. When at the same moment of the ventricular period the base of the ventricle is again stimulated at 2, five connected extrasystoles of the ventricle will appear. Again during each extrasystole a considerable slowing of the conduction is conspicuous and may readily be read from the electrograms. At 3, however, an extra-stimulus touches the base of the ventricle much later, viz. a short time *after* the *T*-deflection. Now only one extrasystole of the ventricle appears. During this extrasystole the rate at which the excitation wave is conducted through the ventricle is very likely slower than during the periodic ventricular systoles, but decidedly not so slow as with the preceding "gehäufte" extrasystoles [1]).

The *R*-deflection is not nearly so broad as in the ventricular electrograms of the "gehäufte" extra-systoles.

We also see at a glance the far slower conduction of the excitation wave during the "gehäufte" extrasystoles, for if we look at the *R*-deflections of the electrograms, it strikes us that the ascending lines are very clearly visible during the "gehäufte" systoles, while both during the periodic ventricular systoles and during the extrasystole at 3 they are reproduced by much thinner lines [2]). This implies that during the "gehäufte" extrasystoles the excitation wave is transmitted at a much slower rate from the starting point through the base of the ventricle than during the periodic ventricular systoles and the extrasystole at 3. It is evident, therefore, that during the extra-

[1]) If we wish to compare the rate of the conduction of the excitation wave, it is evident that we can compare the extrasystole at 3 only with the first systoles of the "gehäufte" ventricle-systoles, for only with them the stimulus starts from a definite point i.e. the same point of the surface of the ventricle (viz. where the stimulant electrode stands).

[2]) In the electrograms of frogs' hearts it usually appears also, when the conduction of excitation has been slackened, that the descending line of the R-deflection is very steep or rather steep. In that case the ascending line of the R-deflection is less steep.

systole at 3 the rate of the conduction of excitation wave is not nearly so much diminished as with the first systole of the "gehäufte" ventricular systoles. Besides, the duration of the electrogram of the extrasystole at 3 is longer than that of the first electrograms of the "gehäufte" extra-systoles. The quicker conduction as well as the longer duration of the ventricle-electrogram, i.e. the longer duration of the refractory stage, contribute to the fact that after the stimulus at 3 only one extrasystole reveals itself. After the quicker conduction the excitation wave is checked by the longer refractory stage.

We see then that the same rule holds for the origin of "gehäufte" extrasystoles and for that of ventricular fibrillation. When the stimulus meets the ventricle directly after the close of the refractory stage, the "gehäufte" extra-systoles can come forth. But when in a frog's heart that exhibits "gehäufte" systoles after being given an electric stimulus directly after the close of the refractory stage, the stimulus is applied at a later time of the ventricle period at the same spot and with the same force, one single extrasystole will appear.

It appears therefore that the "gehäufte" extrasystoles originate only when the metabolic condition of the ventricle is bad, and consequently the excitation wave is conducted slowly through the ventricle. At the moment when the metabolic condition of the ventricle is bad, a stimulus will also evolve a brief extrasystole with a brief refractory stage. The appearance of the "gehäufte" extrasystoles, therefore, is aided as well by the slow conduction of excitation as by the short duration of the refractory stage. Then after the first course through the ventricle which is of long duration, the excitation wave can go round once more, because the starting point has become excitable again at that moment. This may be repeated several times. The conditions for the origin of the "gehäufte" extra-systoles are therefore the same as for the origin of ventricular fibrillation. The mechanism of the processes at work in the ventricular muscle during fibrillation and the "gehäufte" extrasystoles, displays only differences in degree. In the case of both deviations from the normal rhythm the conduction of excitation wave has largely slackened and the duration of the refractory stage has decreased with its appearance. In the case of delirium cordis the excitation wave passes through the ventricle so slowly that every time different muscular areas of the ventricle are made to contract, so that the excitation wave proceeds through the ventricle *slowly* and *by jerks*. This leads to fractionated ventricular systoles, which are linked together for the time of the delirium. During the "gehäufte" extrasystoles, however, the refractory stage is also shortened at the moment of its origin, *but now the excitation spreads*

through the ventricle, slowly indeed, but undisturbed i. e. without shocks. This produces co-ordinated contractions of the ventricular muscle [1]).

The relationship between cardiac fibrillation and "gehäufte" extrasystoles may also appear from the fact that these forms are interchangeable: "gehäufte" extrasystoles may pass into ventricular fibrillation and conversely ventricular fibrillation may pass into "gehäufte" extrasystoles. I will confine myself here by reproducing only an instance of the latter transition forms.

Fig. 4 gives the suspension curves and the electrograms of a frog's heart after bleeding. At 1 an electric stimulus reaches the ventricular base a little past the summit of the *T*-deflection. This induces ventricular fibrillation, ending in an extra-systole. During this fibrillation the auricles continue their pulsations regularly and are delineated in the suspension-curve as slight elevations (marked by the letter A). The appearance of an extrasystole at the termination of a fibrillation of the ventricle is a common phenomenon. Anyhow my curves frequently bore this out.

After the preceding discussion this can be readily accounted for. I also often observed that fibrillation ended in a strong rise of the suspension-curve, which is illustrated in the curves of the first part of this communication and in my paper in Pflügers' Archiv [2]). This marked rise at the end of the fibrillation curve points to a contraction of a rather large area of the heart muscles as the final phase of fibrillation. Upon this the excitation will readily rebound. The same explanation holds for the extrasystole with which fibrillation often concludes. After the extrasystole a prolonged pause appears and after this the normal rhythm ensues. I wish to draw attention to one more particular. Between the fibrillation and the extrasystole a small negative deflection occurs (indicated by an arrow).

It is impossible to say for sure how this deflection has originated. It may be that after the fibrillation a retrograde excitation conduction has given rise to an auricular contraction, which at that moment coincides in the suspension-curve with the extrasystole curve. Then

[1]) It stands to reason that in the case of this strongly retarded conduction of the excitation every ventricular contraction of the "gehäufte" extrasystoles is no of necessity a contraction of the whole ventricular muscle. No doubt partial asystoles especially of the ventricular apex will occur during various "gehäufte" extrasystoles. So much anyhow appears from the figures reproduced by me. Of several "gehäufte" extrasystoles of these figures the negative T-deflections are smaller than may be anticipated from the considerably retarded conduction. It is most probably brought about by the partial apex-asystole.

[2]) Pflügers Archiv. Bd. 178. Seite 1.

we should recognize a negative *P*-deflection, since the excitation wave proceeded in a retrograde direction through the auricles.

Secondly it may be imagined that this negative deflection is generated by a bulbus-contraction. We notice these bulbus electrograms

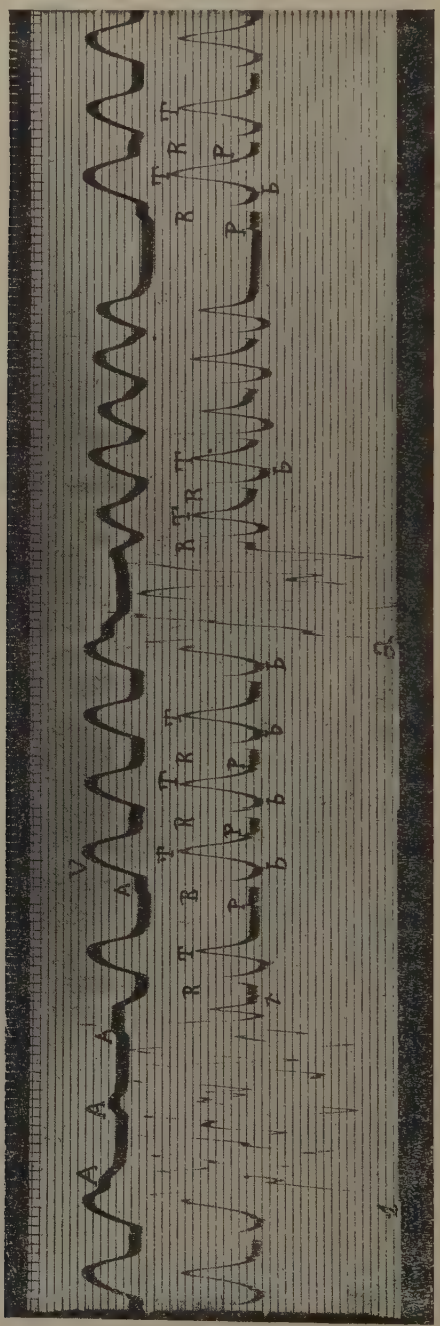

Fig. 4

during the ventricular electrograms of the periodic ventricular systoles and also during the electrograms of some "gehäufte" extrasystoles (indicated in the figure by a b). Then the excitation wave would appear to have spread after the fibrillation over the bulbus arteriosus.

At 2 the ventricular base is stimulated again a little past the summit of the T-deflection. Again ventricular fibrillation is the consequence, while the auricles continue to pulsate in the undisturbed rhythm. After a short time, however, fibrillation passes into five "gehäufte" extrasystoles, followed by a prolonged pause [1]).

Subsequently the normal rhythm recovers itself. In what manner this transition occurs will be further examined by me. It has already appeared that the one process in the ventricle is liable to merge into the other, but also that this transition can occur indirectly. This will be recorded afterwards.

We see then that ventricular fibrillation and "gehäufte" extrasystoles, which are of the same genesis, may even pass into one another. It has thus been proved experimentally that the two rhythm-disturbances are closely allied. This conception has been advocated already by clinicians as WENCKEBACH and LEWIS.

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[1]) It is remarkable that this pause is of a longer duration than the one after the single extrasystole with which the previous fibrillation concluded. The post-extra-systolic pause then is very different as to duration (see also figs 1, 2 and 3) just as the post-undulatory pause, which may even fail altogether. To this I purpose to revert in a later publication.

Physiology. — *"Factors which are of importance for the habit-formation of birds. I. Visual sensations"* [1]). By Miss LUCIE W. SCHUT. (Communicated by Prof. G. VAN RIJNBERK.)

(Communicated at the meeting of June 26, 1920).

Introduction.

In 1918 [2]) BUIJTENDIJK described experiments on habit-formation in birds. He found that a siskin very soon learns to look for food in a seed-box, where the food is hidden from sight by a flap. When this box is placed amongst similar, but empty ones, the bird invariably will go to the filled box, provided it is always kept in the same place amongst the others. The habit formed in this way was not forgotten, even after the bird having been taken for months to other surroundings, for on its return, placed in front of the same boxes, the bird at once flew to its old box for food.

Control and corroboration of BUIJTENDIJK'S *results.*

I repeated the experiments made by BUIJTENDIJK and arrived at the same results as he did. The birds I selected for the experiments were the siskin (Fringilla spinus, 3 specimens), the redcap (Fringilla carduelis, 2 specimens), the paradise widow (Steganura paradisea, 2 specimens) and the Napoleon weaver (Pyromelana afra, 2 specimens). It is surprising how rapidly all these birds, but above all the siskin, learned to push their heads under the flap of the food-box. The siskins accomplished the task at the first trial, within fifteen minutes. The others took a little longer, the experiment having to be repeated regularly for a few days in succession. If, further, I replenished one particular box, placed amongst four similar ones, from the very beginning, as the rule was, the birds were equally quick in learning to look for food in that special box and rarely tipped up the flaps of the other boxes. BUIJTENDIJK believes that the fixed place the feeding-box takes amongst the others, is the ruling element in this case.

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[1]) After experiments made in the physiological Laboratory of the University of Amsterdam.

[2]) F. J. J. BUIJTENDIJK. Proeven over gewoontevorming bij dieren. Amsterdam 1918.

I can corroborate this in principal. In a great number of experiments taken with a siskin I endeavoured to remove every possible mark which might have led the bird to the right box. To this purpose I covered the frontside of the boxes, as also the bottom of the cage in front of them with strips of cardboard, which were constantly renewed. Husks of the eaten seed were carefully cleared away each time and the flaps of the boxes were renewed each time, in order that the bird might not be able to tell it by scratches it might have made with its beak. In spite of these precautions, the bird, once having learned that its food was placed in one particular box, rarely lifted the flap of another by mistake. As a positive proof, in connection with the supposition that the birds were led by other characteristics than the fixed place of the food box, I relate the following experiment: When the siskin had duly learned to go for its food to one particular box, I took a second cage, in all respects similar to the one in which the experiments had been made. This cage was perfeetly new and the siskin had never been in it before. To this cage I had four new foodboxes attached, exactly like the four which up till that moment had been used for the experiments. The siskin had never eaten from these boxes, nor had they ever contained any seed. I now removed the siskin for a short time, on different days, from cage 1 to cage 2. No seed had been put into any of the boxes in order to avoid that the bird should smell the seed behind the flaps. It was evident that the bird felt strange in its new cage; it flew about continually, coming up close to the food boxes, without however lifting up any of the flaps. After it had quieted down a little, the bird, though it certainly made more mistakes in its new cage than in the usual experimental cage, nevertheless sometimes immediately after leaving cage 1 for cage 2, flew to the right box and tipped up the flap.

From this series of experiments I believe I am justified in forming the conclusion that the place the food-box takes is undoubtedly of great significance in the formation of habits. At the same time however I thought it possible that other impressions contributed to the result as well. I therefore decided to find out in how far it was possible to train the birds by means of another factor of impressions.

Other factors which may assist in forming a habit.

I have endeavoured to eliminate the factor of place entirely from the series of experiments, which I will now proceed to give. This was done by filling a different box with food each time, and thus

preventing the bird from becoming accustomed to a fixed spot for its food-box (for this purpose I employed siskins exclusively). I now however gave the food-box a visible mark, to distinguish it from the empty ones.

1. First of all, I pasted black paper over the flap of the food box, the remaining ones being of bright tin. In a few minutes the bird had learned that the seed was behind the black flap. And in an astonishing short space of time a bird that has first been trained to look for the seed box, according to its position, seems to have forgotten this and it learns that the seed is behind the black flap. By repeatedly hanging this in front of another box, the bird is literally taught to fly after this black flap and exclusively or almost so, to tip up this flap to look for its food [1]).

2. In a second series of experiments the flap of the food-box was pasted over with a blue paper. The flaps of the remaining empty boxes were also pasted over with blue paper, with blue of a different shade however. The result was that in a relatively short space of time the bird had learned again to go for its food to the box with the flap pasted over with blue of a particular shade, distinguishing it from the remaining flaps. The difference was scarcely perceptible: in a series of experiments I used blue N°. 1186 of the well-known coloured papers of BAUMANN for the empty boxes, and N°. 1187 for the food box (food-colour) [2]), this difference is barely perceptible to the human eye. (1187 is the merest shade darker).

3. A series of controls was still taken with green papers of different shades. It appeared that the siskin distinguished as food colour N°. 985 from green N°. 984, from BAUMANN's scale.

4. In a subsequent series of experiments I selected an extremely small token of distinction for the food box. The flaps of all four boxes were pasted over with white paper, but on the flap of the food box a small round black disc was stuck in the centre.

Here again it was observed that it was comparatively easy by hanging the flap with the black food-token before another box each time, to teach the siskin, to look for its food exclusively behind the flap with the black disc.

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[1]) In fact the bird had by no means forgotten the first learned token of locality. I will revert to this point in the exhaustive paper to be issued soon. For the rest, experiments were frequently made with blank specimen, (empty boxes), to prevent use of smell interfering.

[2]) As is known, birds according to HESS do not see spectral colours further than the line of demarcation between green and blue. The difference detected must therefore be due to a difference in the shade.

5. Encouraged by the result of the series of experiments described so far, I resolved on employing a more subtle mark of distinction. I again employed white flaps for my purpose. The empty boxes had a black square, the food box a black disc of about the same size. The result of this series of experiments was not sufficiently convincing. Nevertheless I had the impression, when the siskin went to the box with the round disc, that this was not always entirely a matter of chance.

SUMMARY.

1. The result of my experiments is in corroboration with those of BUYTENDIJK, that the place a food-box takes in the midst of other (empty) boxes, is of great importance for teaching birds to form the habit of eating from that box.

2. In addition there are however numerous other visual factors which may tend to develop this habit.

Chemistry. — *"Two Isomeric Chloro-Tetracetyl-d-Fructoses"*. By Prof. F. M. JAEGER.

(Communicated at the meeting of June 26, 1920).

§ 1. Some time ago Dr. D. H. BRAUNS observed that, when phosphorus pentachloride at low temperatures acts upon *β-tetracetyl-fructose* dissolved in dry chloroform, under differently chosen circumstances, *two* compounds are formed in the reaction, which both have the composition of a *chloro-tetracetyl-fructose*, but which differ considerably in properties. The one isomeride: *α-chloro-tetracetyl-d-fructose*, melts at 83° C., and has a specific rotation of $[\alpha]_D^{20^\circ} = -160^\circ,9$ (the maximum value measured in chloroform-solution); it is produced only, if *aluminiumchloride* be added to the reaction-mixture as a catalyst. Contradictory to what one might perhaps expect beforehand from this mode of preparation, this *α*-derivative appears to be unstable to such a degree, that it is decomposed into an impure *β-tetracetyl-fructose* and an acid liquid within twenty-four hours, if exposed to the air at room-temperature. Only if preserved in the dark in an ice-box at a temperature of 0° C,, it appeared possible to recrystallize the substance repeatedly from dry ether, if moisture be excluded as carefully as possible; even then, however, the decomposition mentioned above finally sets in. On the other hand, the other isomeride: *β-chloro-tetracetyl-d-fructose*, which is produced under the same circumstances, if only *no* catalyst be added to the mixture, appears to be a very stable substance in comparison with the labile *α*-derivative, and may be recrystallized from most of the organic solvents, without being changed to any appreciable degree. It melts at 108° C., and has, in chloroform-solution, a specific rotation of $[\alpha]_B^{20^\circ} = +45^\circ,2$. While the *α*-compound has an intensely bitter taste, the *β*-derivative tastes only feebly bitter, and it is considerably more soluble in most solvents than the *α*-isomeride. The *β*-compound is also not absolutely stable: when repeatedly recrystallized from absolute alcohol, the formation of ethylacetate can be observed; and when solutions in commercial benzine are slowly evaporated at 18° C., the crystals obtained appear to be slightly coloured pink, while the mother-liquid also assumes a gradually increasing violet or even brown colour. In comparison with the *α*-compound, however, it can be considered to be "stable"; as far as known, these two

isomerides can*not* be transformed directly into each other. A 0,1 normal solution of $NaOH$ causes all the chlorine to be split-off from the α-derivative within five hours at 0° C.; the β-derivative, however, does not liberate its chlorine under the same circumstances. The determinations of carbon, hydrogen, and chlorine (Carius), and those of the molecular weight, gave with both substances the same results, all agreeing with the composition of a *chlorotetracetyl-fructose*: $C_6H_7O(C_2H_3O_2)_4Cl$.

§ **2.** In connection with the measurements of the isomeric α- and β-*pentacetyl-* [1]), and *tetracetyl-d-fructoses* [2]) formerly made by the author, it appeared of interest to study these two isomerides also from a crystallographical point of view, and to compare them with each other, as well as with the derivatives mentioned above. Chiefly with respect to the instability of the α-derivative, it was necessary, therefore, to prepare both isomeric substances once more, and immediately to measure the crystals eventually obtainable under favourable circumstances. This was possible to me by Mr. Braun's kind assistance, who placed a quantity of the β-*tetracetyl*-derivative already described at my disposal, as well as his notes about the method of preparation of the chloro-derivatives. I wish to express to him also here my sincere thanks for his interest and help.

The preparation, especially of the α-compound, must be carefully supervised; it is not so easy as it might perhaps appear to be. More particularly, the *tetracetyl-fructose* used must be free from acid, and the reagents applied may not contain moisture, nor may appreciable changes of temperature occur during the reaction. It is desirable to work very rapidly: therefore, the evaporation of the solutions must take place under a glass bell-jar connected with a drying apparatus by blowing over the surfaces air carefully dried with calciumchloride. The α-compound can best be recrystallized from dry ether in the ice-box at 0° C., and in darkness, moisture being carefully excluded. The same precautions should be taken in preparing the β-isomeride; but the substance may be recrystallized in the usual way at roomtemperature. Purification of the β-compound can best be done by recrystallizing it from boiling absolute alcohol; to obtain beautiful and measurable crystals, the substance is dissolved in pure benzene, or in a mixture of chloroform and benzene, from which it is deposited on slow evaporation in big, transparent, prismatic

[1]) F. M. Jaeger Proceed. R. Acad. of Sciences, Amsterdam, **20**, 280, (1918).

[2]) F. M. Jaeger. Proceed. R. Acad. of Sciences, Amsterdam, **10**, 563, (1908); Zeits. f. Kryst. und Miner., **45**, 539, (1908).

crystals, possessing about the same refractive index as the remaining mother-liquor, and, therefore, being almost invisible in it.

Preparation of α-Chloro-tetracetyl-d-Fructose.

30 Grams of freshly recrystallized and carefully dried *β-tetracetylfructose* are dissolved in 90 ccm. dry chloroform in a glass bottle with ground stopper; the solution is cooled to 0° C. by means of ice. Now *first* 7,5 grams of finely powdered, dry Al_2Cl_6 is added, and *afterwards* 19 grams of dry phosphoruspentachloride. When all is at 0° C., the vessel is removed from the ice-bath, and the mixture is left at room-temperature for 30 minutes, while it is stirred from time to time and while an opportunity is given to the vapours of the hydrochloric acid formed and to those of the chloroform to escape. Then the bottle is placed once more into the ice, the contents of it, after being cooled rapidly, brought into a separating funnel, and the liquor rapidly washed with a solution of sodium-bicarbonate cooled with pieces of ice; finally it is again washed with some ice-water. The chloroform-solution is subsequently dried by means of coarsely grained anhydrous $CaCl_2$, and the dry solution, after being filtered, rapidly evaporated in a wide crystallisation-dish by means of a strong current of dry air, under a glass bell connected with drying apparatus. The very viscous mother-liquor gets finally crystallized; crusts of solid matter are deposited, which are put upon a hard filter, rapidly sucked-off, the crystals pressed between sheets of filterpaper, and dissolved in dry ether. In the ice-box colourless needles or thicker prisms were gradually deposited from the solution, which, if suited for measurements, must be investigated immediately. All necessary precautions being taken, the reaction yields about 60—65 % of the theoretical quantity.

Preparation of β-chloro-tetracetyl-d-fructose. The preparation of this isomeride occurs just in the same way as that of the α-derivative, only *no* Al_2Cl_6 being added to the solution. After the chloroform has been evaporated, a small quantity of absolute alcohol is added, by which immediately an aggregation of colourless needles is formed, which is treated as described above and then repeatedly recrystallized from boiling absolute alcohol. Measurable crystals are best obtained from benzene; the substance crystallizes in short, thick prisms, the α-isomeride (from ether) in more tiny, colourless needles. In both cases a yield of about the same percentage may be obtained.

§ 3. **α-Chloro-tetracetyl-d-fructose** (mpt. 83° C.) crystallizes from dry ether at 0° C. in the shape of small colourless and transparent needles, the end-faces of which are often only rudimentarily developed.

They are *rhombic*, most probably *bisphenoïdical*, with the parameters: $a : b : c = 0{,}9759 : 1 : 0{,}3284$.

Forms observed: $a = \{100\}$, narrow, but broader than $b = \{010\}$, which form generally is present only with a single, extremely narrow plane; $m = \{110\}$, large and lustrous, commonly yielding multiple reflexes; $r = \{101\}$, giving sharp mirror-images. In the zône

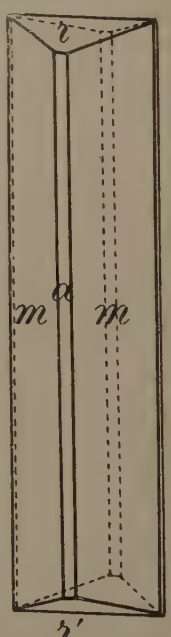


Fig. 1. *α-Chlorotetra-acetyl-d-fructose.*

of the c-axis the angular values are mostly oscillating, the reflexes being multiple; with very thin individuals, however, exact measurements could be made. The aspect of the crystals is that of prisms elongated in the direction of the c-axis. No distinct cleavage was found. The prism-faces (110) and $(\bar{1}\,\bar{1}\,0)$ were much more lustrous and yielded much sharper images than the faces $(1\bar{1}0)$ and $(\bar{1}10)$, which ordinarily were somewhat curved and duller.

Angular Values:	*Observed:*	*Calculated:*
$a : m = (100) : (110) =$*	44 18	—
$r : r = (101) : (\bar{1}01) =$*	37 12	—
$m : b = (110) : (010) =$	45 44	45°42′
$m : m = (110) : (\bar{1}10) =$	91 28	91 24
$a : r = (100) : (101) =$	71 24	71 24
$r : m = (101) : (110) =$	77 10	76 18⅓
$r : m = (101(: (1\bar{1}0) =$	77 2	76 18⅓

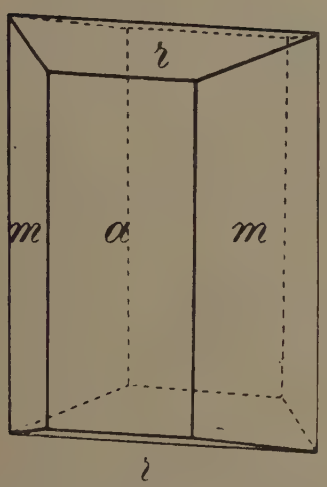


Fig 2 *β-Chloro-tetracetyl-d-Fructose.*

The crystals are positively birefringent. The optical axial plane is {001}; on the prism-faces, just at the border of the field, the emergence of an optical axis is observable. The dispersion has a rhombic character, with $\varrho > v$. The aspect of the crystals is very much like that of the β-derivative.

§ 4. **β-Chloro-tetracetyl-d-fructose** (mpt.: 108° C.) crystallizes from benzene in the shape of large, clear, very lustrous and short prismatic crystals, which with exception of their smaller development in the direction of the c-axis, show an undeniable analogy with the crystals of the α-compound.

Big, colourless crystals, yielding, however, ordinarily multiple reflections, and imperfectly built.

Rhombic-bisphenoïdical.

$$a : b : c = 1{,}7478 : 1 : 0{,}7112.$$

Forms observed: $a = \{100\}$ and $m = \{110\}$, well developed and giving sharp images; $r = \{101\}$, large, eminently reflecting; once a positive bisphenoid, probably $\{523\}$, and very subordinate, was observed, difficultly measurable.

The aspect is short prismatic in the direction of the *c*-axis, occasionally also isometrically developed.

Angular Values:	*Observed:*	*Calculated:*
$a : m = (100) : (110) =$	* 60° 13½′	—
$a : r = (110) : (101) =$	* 67 51½	—
$m : m = (110) : (\bar{1}10) =$	59 33	59° 33′
$r : r = (101) : (\bar{1}01) =$	44 17	44 17
$r : m = (101) : (110) =$	79 10	79 12¾
$o : m = (523) : (110) =$	ca. 50 56	51 51
$o : o = (523) : (\bar{5}\bar{2}3) =$	ca. 48 50	49 12½
$o : o = (523) : (5\bar{2}\bar{3}) =$	117 30	117 0

No distinct cleavage was observed.

§ 5. There is evidently no distinct form-analogy present between the two isomeric *chloro-tetracetyl-d-fructoses*, in contradiction to what was formerly stated in the case of both *α*- and *β-pentacetyl-d-fructoses*. The substitution of a Cl-atom for hydrogen, has evidently, however, not a lowering of the degree of symmetry of the original substances as a consequence, all four acetyl-derivatives being *rhombic-bisphenoidical*. However, from the results obtained, it appears still to be impossible to demonstrate a more intimate analogy of the crystal-forms of the *α*- and *β*-derivatives of this series and that studied formerly.

Laboratory for Inorganic and Physical Chemistry
of the University of Groningen.

Chemistry. — *"On the Crystalforms of some Substituted Amides of Para-Toluenesulphonic Acid."* By Prof. F. M. JAEGER.

(Communicated at the meeting of June 26, 1920).

§ 1. In the following the results are communicated of an investigation concerning the crystallographical properties of a series of substituted *amides* derived from *p-toluene-sulphonic acid* [1]), already prepared by Prof. VAN ROMBURGH in 1902. These preparations, which in general occur in beautiful crystals, were ceded to me a long time ago by the said chemist for the purpose indicated; but the results of these measurements have not been published hitherto.

To colleague VAN ROMBURGH's benevolence I am indebted also for some still lacking data on the specific weight of several of these substances.

In the text occasionally attention has been drawn to some regularities of the crystalforms of these derivatives, which, from a chemical standpoint, are closely related to each other; a review of the numerical data is, moreover, added to this paper at the end. Distinct relations in the crystalforms of these derivatives have, however, not been found in great number, notwithstanding their close chemical relationship.

§ 2. I. Nitro-p-Toluene-sulpho-amide.

This substance, which melts at 141° C., crystallizes from ethyl-alcohol in big, very transparent crystals, which often possess curved

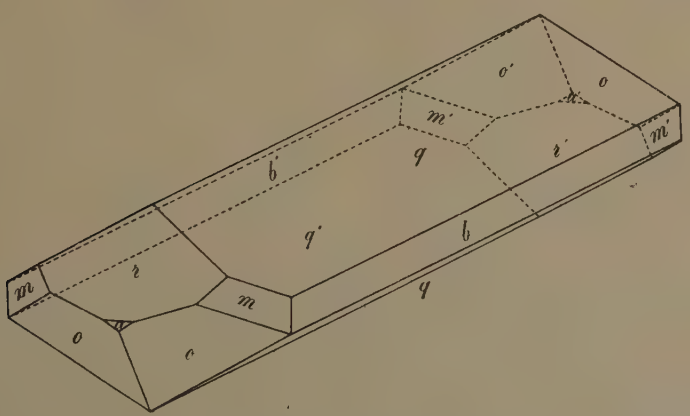


Fig. 1. *Nitro-p-Toluene-sulpho-amide.*

[1]) Cf. also: P. VAN ROMBURGH, Proceed. Acad. of Sciences Amsterdam, Februari, (1902).

faces, making the measurements rather difficult. From ethylacetate we obtained occasionally also great, hexagonally bounded, tabular individuals. The most exact measurements were made with very small, almost colourless crystals, showing very constant angular values.

Although they belong, according to their optical properties, to the monoclinic system, their angle β, however, does not differ from 90°.

Monoclinic-prismatic; pseudo-rhombic.

$a : b : c = 1{,}2289 : 1 : 1{,}1812.$

$\beta = 90°.$

Forms Observed: $q = \{012\}$, predominant and yielding perfect reflexes; $r = \{101\}$, large and strongly reflecting; $m = \{110\}$, smaller, but well developed and lustrous; $b = \{010\}$, narrow and dull, often absent; $o = \{\bar{2}12\}$, well developed and lustrous; $a = \{100\}$, very small and dull, but at least measurable; finally an extremely small pyramid $x = \{\bar{7}11\}$ (?) was observed, which, however, was mostly absent and very badly reflecting. The aspect of the crystals is thick-prismatic parallel to q, with elongation in the direction of the a-axis; however, the crystals are often most irregularly distorted. Ordinarily r is present only with a single face.

Angular Values:	*Observed:*	*Calculated:*
$q : r = (012) : (101) =$*	51°38½′	—
$m : q = (110) : (012) =$*	66 46	—
$q : q = (012) : (0\bar{1}2) =$	61 3	61° 8′
$q : b = (012) : (010) =$	59 29	59 26
$q : a = (012) : (100) =$	90 0	90 0
$o : o = (\bar{2}12) : (\bar{2}\bar{1}2) =$	46 4½	46 8
$o : q = (\bar{2}12) : (012) =$	39 34½	39 37
$o : q = (\bar{2}12) : (0\bar{1}2) =$	67 59	68 10
$m : o = (\bar{1}10) : (\bar{2}12) =$	45 2	45 4
$o : r = (\bar{2}12) : (101) =$	23 4	23 4
$m : q = (110) : (01\bar{1}) =$	66 50	66 46
$a : x = (\bar{1}00) : (\bar{7}11) =$	18 48	19 3

There is a distinct cleavage parallel to $\{010\}$.

Although the angle β does not differ appreciably, the optical properties prove, however, that the compound has monoclinic symmetry: on $\{012\}$ the extinction-angle is about 23° with respect to the a-axis; in the same way the extinction-angle on $\{010\}$ is about 42° with respect to the a-axis. The optical axial plane is probably parallel to $\{010\}$.

The specific weight of the crystals at 15° C. is: 1,612; the equivalent-volume is therefore: 133,99. The topical parameters are calculated to: $\chi : \psi : \omega = 5{,}5537 : 4{,}5194 : 5{,}3383$.

§ 3. Comparing the axial ratio with the parameters of the three isomeric *toluene-sulphonamides* themselves, their form-relationship becomes very clear, if only the interpretation is made somewhat deviating from that given in the literature [1]).

Adopting the symbols of the different combination-forms, as given by WEIBULL, we can give the following survey of the modified data:

Ortho-toluene-sulphonamide; mpt: 156°,3 C. $a : a : c = 1{,}000 : 1 : 1{,}0332$; $\beta = 90°$.
Tetragonal-bipyramidal.
$p = \{110\}$; $v = \{111\}$; $o = \{113\}$; $u = \{313\}$.

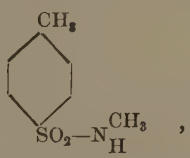
Meta-toluene-sulphonamide; mpt: 108° C. $a : b : c = 1{,}0453 : 1 : 1{,}0333$; $\beta = 88°27\frac{1}{2}'$.
Monoclinic-prismatic; pseudo-tetragonal.
$= \{100\}$; $b = \{010\}$; $m = \{210\}$; $o = \{112\}$; $s = \{\bar{1}12\}$; $\omega = \{122\}$; $r = \{\bar{1}02\}$.

Para-toluene-sulphonamide; mpt: 137°,5 C. $a : b : c = 1{,}2016 : 1 : 0{,}9364$; $\beta = 87°29'$.
Monoclinic-prismatic.
$b = \{010\}$; $p = \{011\}$; $o = \{\bar{3}12\}$; $v = \{310\}$; $r = \{302\}$.

Nitro-p-toluene-sulphonamide; mpt: 141° C. $a : b : c = 1{,}2289 : 1 : 1{,}1812$; $\beta = 90°$.
Monoclinic-prismatic; pseudo-rhombic.
$a = \{100\}$; $b = \{010\}$; $q = \{012\}$; $m = \{110\}$; $r = \{101\}$; $o = \{\bar{2}12\}$.

§ 4. II. p-Toluene-sulpho-methylamide.

This substance, which has the formula:



and which melts at 76° C., crystallizes from alcohol in the form of very thin, transparent, colourless, rectangular little plates.

[1]) M. WEIBULL, Zeit. f. Kryst. u. Miner. **15**, 251. (1889); O. MÜGGE, Diss. Göttingen, (1879), p. 15; cf. also: K. WALLIN and P. KLASON, Ber. d. d. Chem. Ges. **12**, 1851. (1879). The crystals were obtained from alcohol or water. On the binary melting point-curve of *o-* and *p- toluenesulphonamide*, cf. P. V. MC. KIE, Journ. Chem. Soc. London, **113**, 799. (1918).

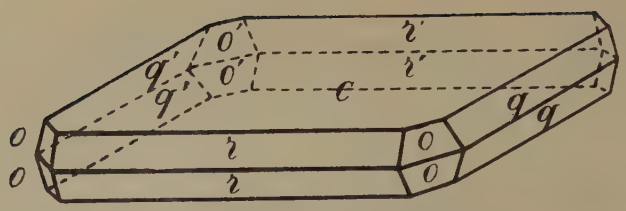


Fig. 2. *p-Toluene-sulpho-methylamide.*

Rhombic-bipyramidal.

$a : b : c = 1{,}0358 : 1 : 2{,}6074.$

The crystals represent evidently pseudo-tetragonal limiting forms; also optically they approach to tetragonal symmetry.

Observed Forms: $c = \{001\}$, very lustrous, predominant, giving splendid reflexes; $r = \{101\}$, and $q = \{011\}$, almost equally broad, well reflecting; $o = \{121\}$, small, dull, and difficult to measure accurately. The aspect of the crystals is thin tabular parallel to $\{001\}$, often with a slight elongation in the direction of the *b*-axis.

Angular values:	*Observed:*	*Calculated:*
$c : r = (001) : (101) =$*	68°20′	—
$c : q = (001) : (011) =$*	69 1	—
$r : r = (101) : (10\bar{1}) =$	43 20	43°20′
$q : q = (011) : (01\bar{1}) =$	41 58	41 58
$c : o = (001) : (121) =$	80 25	80 12
$o : o = (121) : (12\bar{1}) =$	18 10	18 36

Cleavage parallel to $\{001\}$.

The plane of the optical axes is $\{100\}$, *c* being 1st bisector. The apparent axial angle is very small, the crystals approaching also in this respect to uniaxity.

The specific gravity of the crystals at room-temperature was: $d_4° = 1{,}340$; the molecular volume is therefore: 138,06, and the topical parameters become: $\chi : \psi : \omega = 3{,}8442 : 3{,}7113 : 9{,}6770$.

§ 5. III. Nitro-p-Toluenesulpho-methyl-amide.

This compound is derived from the first by substitution of a hydrogen-atom of the NH_2-group by CH_3. From ethylacetate the substance crystallizes in beautiful, pale yellow prisms, and melts at 91° C. The crystals are generally dull and not easily measurable.

Monoclinic-prismatic.

$a : b : c = 1{,}0522 : 1 : 0{,}3948;$

$\beta = 86°40\frac{1}{2}.$

Forms Observed: $m = \{110\}$, the largest developed of all forms; $a = \{100\}$, narrow, and $r = \{101\}$ yet smaller; $o = \{111\}$, small, but yielding good reflexes.

The aspect of the crystals is that of long needles or prisms parallel to the c-axis.

Angular Values:	*Observed:*	*Calculated:*
$m : a = (110) : (100) =$*	46°24½′	—
$o : o = (111) : (1\bar{1}1) =$*	71 52	—
$m : o = (\bar{1}10) : (111) =$*	78 18	—
$m : o = (110) : (111) =$	49 35	49°39½′
$m : m = (110) : (1\bar{1}0) =$	87 11	87 11
$c : m = (001) : (110) =$	—	87 42½
$r : o = (101) : (111) =$	35 58	35 56

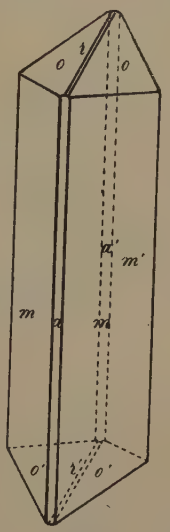


Fig. 3. *Nitro-p-toluene-sulpho-methyl amide.*

Perfectly cleavable parallel to $\{101\}$.

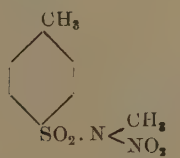
As the crystals were in every case dull and curvi-planed, more exact measurements appeared almost illusory.

The extinction on a was normally, on m obliquely orientated with respect to the edge $a : m$.

The specific weight of the crystals was: 1,485 at 16° C.; the equivalent-volume is, therefore: 154,21, and the topical axes are calculated at: $\chi : \psi : \omega = 7{,}5664 : 7{,}1910 : 2{,}8390$.

§ 6. IV. p-Toluene-sulpho-methylnitramide.

This compound, which possesses the structure:



and melts at 60° C., crystallizes from a mixture of ligroin and ether in almost colourless flat needles, or in thick, short prisms. They are well built and give good reflexes.

Monoclinic-prismatic.

$a : b : c = 1{,}3210 : 1 : 0{,}6892$;

$\beta = 78°6'$.

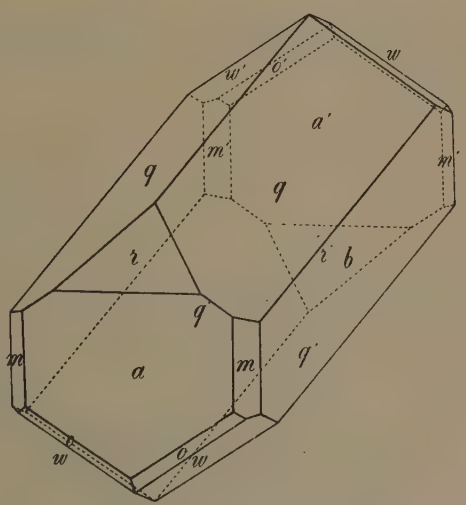


Fig. 4. *p-Toluene-sulpho-ethylnitramide.*

Forms Observed: $q = \{011\}$, large and very lustrous; $a = \{100\}$, large, mostly with one rudimentary face, but yielding good reflexes; $b = \{010\}$, narrower, sometimes curved; $r = \{101\}$, great and lustrous; $m = \{110\}$, perfectly reflecting; $\omega = \{\bar{1}11\}$, mostly narrow, but in the needle-shaped individuals as large as m, while r is here lacking in most cases; finally $o = \{\bar{3}11\}$, often well developed. The aspect of the crystals is thick prismatic, with a slight elongation parallel to the a-axis; rarely needles parallel to the same axis.

Angular values:	*Observed:*	*Calculated:*
$q : q = (011) : (0\bar{1}1) =$*	67°59½′	—
$q : a = (011) : (100) =$*	80 9	—
$a : m = (100) : (110) =$*	52 14½	—
$q : b = (011) : (010) =$	56 0	56° 0′
$a : r = (100) : (101) =$	53 14	53 21
$q : r = (011) : (101) =$	41 14	41 9
$b : m = (010) : (110) =$	37 44	37 45½
$a : w = (100) : (\bar{1}11) =$	74 49	75 2
$w : q = (\bar{1}11) : (011) =$	25 1	24 49
$a : o = (100) : (\bar{3}11) =$	40 50	40 58
$o : q = (\bar{3}11) : (011) =$	59 1	58 53

No distinct cleavage was found.

The extinction-angle on $\{010\}$ is 31° with respect to the a-axis.

The specific weight of the crystals is: 1,454 at room-temperature; the equivalent-volume is thus: 165,06, and the topical axes are calculated at: $\chi : \psi : \omega = 7{,}5309 : 5{,}7009 : 3{,}9291$.

§ 7. V. p-Toluene-sulpho-ethylamide.

This compound, which melts at 64° C., has the structure:

It crystallizes from a mixture of absolute alcohol and ether in colourless, parallelogram-shaped, thin plates, or small prismatic crystals. The solutions have a tendency to supersaturation.

Triclinic-pedial

$a : b : c = 0{,}6481 : 1 : 0{,}4136$;

$\alpha = 77°39\frac{1}{2}$; $A = 77°37\frac{1}{3}$

$\beta = 88°6'$; $B = 88°21\frac{1}{2}'$.

$\gamma = 102°55\frac{1}{2}$; $C = 102°53\frac{1}{2}$.

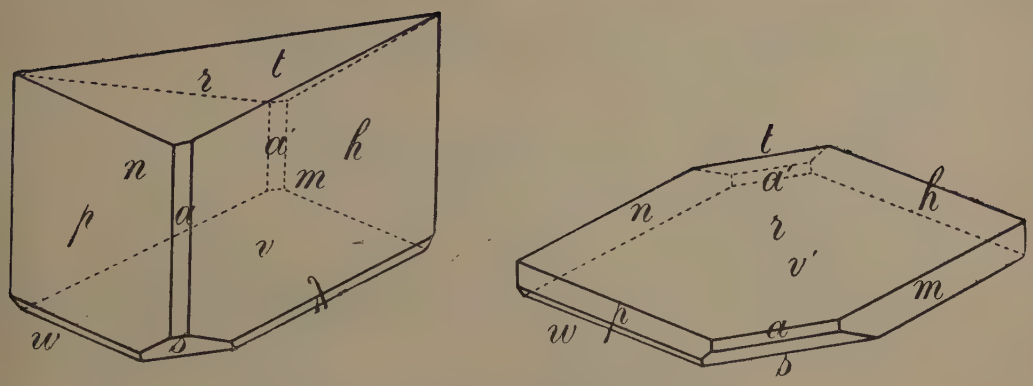


Fig. 5. *p-Toluene-sulpho-ethylamide.*

Forms observed: $r = \{101\}$ and $v = \{\bar{1}0\bar{1}\}$, large and very lustrous, mostly predominant, the crystals therefore being often tabular parallel to these planes; $t = \{\bar{1}01\}$, also lustrous, somewhat smaller than r and v; $s = \{10\bar{1}\}$, smaller than t, and showing commonly a fine striation parallel to the edge $s:v$; $a = \{\bar{1}00\}$ and $a' = \{100\}$, narrow, but well reflecting; $m = \{110\}$, large, always showing a striation parallel to the edge $m:r$; $p = \{\bar{1}10\}$, $n = \{\bar{1}\,\bar{1}\,0\}$, and $h = \{\bar{1}\bar{1}0\}$, large and highly lustrous; $\omega = \{1\,\bar{2}\,\bar{1}\}$ and $\lambda = \{12\bar{1}\}$, very narrow and badly reflecting, λ generally striated parallel to $m:v$; probably again $q = \{0\bar{1}\bar{1}\}$, very small and commonly not measurable. The aspect of the crystals is tabular parallel to r, or thick prismatic towards the c-axis. A cleavage occurs parallel to $\{101\}$.

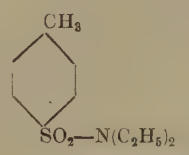
Angular Values:	*Observed:*	*Calculated:*
$a:r = (100):(101) =$*	58°34′	—
$a:s = (100):(10\bar{1}) =$*	56 14	—
$a:p = (100):(\bar{1}10) =$*	37 11	—
$a:m = (100):(110) =$*	29 23	—
$r:p = (101):(\bar{1}10) =$*	58 17	—
$r:t = (101):(\bar{1}01) =$	65 18	65°12′
$s:v = (10\bar{1}):(\bar{1}0\bar{1}) =$	65 10	65 12
$s:p = (10\bar{1}):(\bar{1}10) =$	70 40	70 24
$s:m = (10\bar{1}):(110) =$	56 39	56 37
$r:m = (101):(110) =$	68 24	68 35½
$w:p = (1\bar{2}\bar{1}):(\bar{1}10) =$	51 2	51 13

On all faces the optical extinction occurs obliquely with respect to the borders: on r about 46° with respect to the edge $r:p$; on p about 36°, on a about 43°, on m about 34° with respect to the direction of the c-axis. On r and p is the emergence of an optical axis observable, excentrically in the field of the microscope.

The specific gravity of the crystals is 1,307; the equivalent-volume therefore: 152,26, and the topical parameters become: $\chi : \psi : \omega = 4{,}6805 : 8{,}4202 : 3{,}4825$.

§ 8. VI. p-Toluene-sulpho-diethylamide.

This compound having the structure:



and melting at 59° C., crystallizes from a mixture of absolute alcohol and ethylacetate in the shape of thin, colourless, hexagonally bordered little plates, or in somewhat thicker tabular, and often opaque crystals.

Monoclinic-prismatic.

$a : b : c = 1{,}0149 : 1 : 0{,}6762$;

$\beta = 72°1'$.

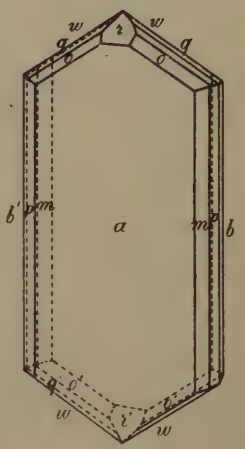


Fig. 6. *p-Toluene-sulpho-diethylamide.*

Observed Forms: $a = \{100\}$, predominant and very lustrous; $o = \{111\}$, $q = \{011\}$, $m = \{110\}$, $p = \{120\}$, all about equally broad and yielding splendid reflexes; $r = \{101\}$, very lustrous, well developed; $\omega = \{\bar{1}11\}$, somewhat narrower than o, but yielding also sharp images; $n = \{210\}$, and $b = \{010\}$, extremely narrow, often absent and giving feeble reflexes. The crystals are well built, and allow exact measurements. Their aspect is tabular parallel to a and elongated in the direction of the c-axis. The crystals are very brittle.

Angular values:	*Observed:*	*Calculated:*
$a : o = (100) : (111) =$*	49°40′	—
$a : q = (100) : (011) =$*	74 57	—
$a : r = (100) : (101) =$*	44 17½	—
$o : q = (111) : (011) =$	25 17	25°17′
$q : \omega = (011) : (\bar{1}11) =$	32 18	32 20½
$\omega : a = (\bar{1}11) : (\bar{1}00) =$	72 45	72 42½
$o : r = (111) : (101) =$	25 15	25 17
$b : o = (010) : (111) =$	64 45	64 43
$a : m = (100) : (110) =$	43 58½	43 59½
$m : p = (110) : (120) =$	18 34	18 32½

Angular values:	*Observed:*	*Calculated:*
$p : b = (120) : (010) =$	27 23	27 23
$b : m = (010) : (110) =$	46 2	46 0½
$a : n = (100) : (210) =$	26 9	25 46
$n : m = (210) : (110) =$	17 59	18 13½
$a : p = (100) : (120) =$	62 31	62 37

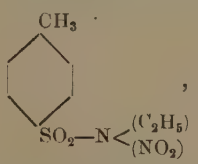
No distinct cleavage was found.

The optical axial plane is {010}. Very strong, inclined dispersion, with $\varrho < v$; on {100} one axis emerges excentrically in the field of the microscope.

The specific weight of the crystals at 15° C. was: 1,230; the equivalent-volume is therefore: 184,55, and the topical parameters are calculated to: $\chi : \psi : \omega = 6{,}6611 : 6{,}5633 : 4{,}4381$.

§ 9. VII. p-Toluene-sulpho-ethylnitramide.

This substance, which has the configuration:



crystallizes from ether in big, colourless crystals, or in hexagonally-shaped tables. It melts at 69° C.

Monoclinic-prismatic.

$a : b : c = 1{,}0178 : 1 : 1{,}1005$;

$\beta = 88°11'$.

Forms Observed: $c = \{001\}$, strongly predominant and lustrous; $a = \{100\}$, sometimes large, often also narrower, but always yielding sharp reflexes; $m = \{130\}$, well developed, but often with curved faces and somewhat dull; $r = \{\bar{2}03\}$, well reflecting, often absent; $\omega = \{\bar{1}33\}$, extremely narrow, in most cases absent, and only approximately measurable. The aspect of the crystals is either short prismatic with an elongation parallel to the *b*-axis, or thin lamellar parallel to {001}.

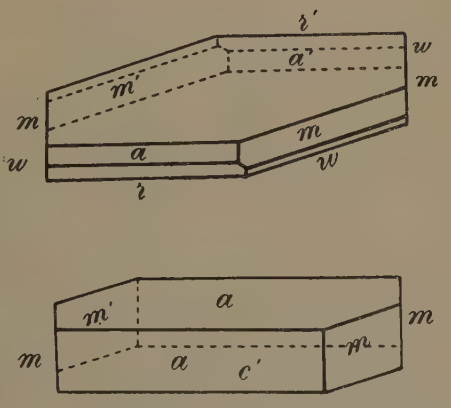


Fig. 7. *p-Toluene-sulpho-ethylnitramide.*

Angular Values:	*Observed:*	*Calculated:*
$a : c = (100) : (001) =$	* 88°11′	—
$a : m = (100) : (130) =$	* 71 51½	—
$a : r = (100) : (20\bar{3}) =$	* 55 25	—
$c : r = (001) : (\bar{2}03) =$	36 24	36 24
$m : m = (130) : (1\bar{3}0) =$	36 27	36 17
$c : w = (001) : (\bar{1}33) =$	50 8	49 29
$m : w = (\bar{1}30) : (133) =$	40 58	41 5
$c : m = (001) : (130) =$	89 24	89 26

Very perfectly cleavable parallel to {001}.

On *a* and *c* the extinction is normally orientated, but often of undulatory character, as the result of geometrical anomalies in the structure of the crystals.

The specific gravity of the crystals was 1,450; the equivalent-volume is therefore: 168,27, and the topical parameters become: $\chi : \psi : \omega = 5{,}4115 : 5{,}3169 : 5{,}8513$.

§ 10. VIII. Nitro-p-Toluene-sulpho-ethylnitramide.

This substance, which melts at 76° C., can only rarely be obtained in measurable crystals. Those here investigated were deposited from a hot saturated solution in carbon tetrachloride by very slow evaporation.

Thin, yellow, very lustrous and transparent plates, commonly with hemimorphic development (fig. 8).

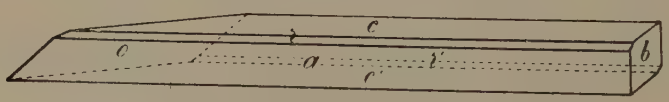


Fig. 8. *Nitro-p-Toluene-sulpho-ethyl-nitramide.*

Monoclinic, probably *sphenoidical.*

$$a : b : c = 0{,}4812 : 1 : 0.8766;$$

$$\beta = 85°5'.$$

Forms Observed: $c = \{001\}$, predominant, and very lustrous, $o = \{\bar{1}\bar{1}1\}$, yielding ideal reflexes, often with only a single plane; $a = \{100\}$, giving good mirror-images; $b = \{010\}$, often absent, but otherwise well reflecting: $r = \{705\}$, very narrow, often totally absent. The crystals often show oscillatory angular values, principally in the zône of the orthodiagonal, and multiple reflexes. The aspect is tabular parallel to {001}, and strongly elongated towards the *b*-axis.

Angular values:	*Observed:*	*Calculated:*
$c : a = (001) : (100) =$*	85° 5′	—
$c : o = (001) : (\bar{1}1\bar{1}) =$*	67 16	—
$a : o = (\bar{1}00) : (1\bar{1}\bar{1}) =$*	37 21	—
$c : r = (001) : (705) =$	64 42	64°23′
$r : a = (705) : (100) =$	20 16	20 42
$c : b = (001) : (010) =$	89 52	90 0
$o : r = (\bar{1}1\bar{1}) : (\bar{7}05) =$	54 23	54 24

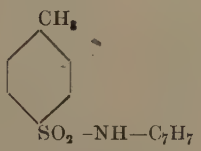
No distinct cleavage was found.

The optical axial plane is parallel to {010}; on c and a both an optical axis emerges excentrically.

The specific weight of the crystals is: 1,555; the equivalent-volume therefore: 156,91, and the topical parameters are calculated at: $\chi : \psi : \omega = 3{,}4652 : 7{,}2001 : 6{,}3119$.

§ 11. IX. p-Toluene-sulpho-benzylamide.

Structure:



From a mixture of ether and alcohol the compound crystallizes in large, colourless crystals with varying aspect. It melts at 113° C. The crystals are well built and allow exact measurements.

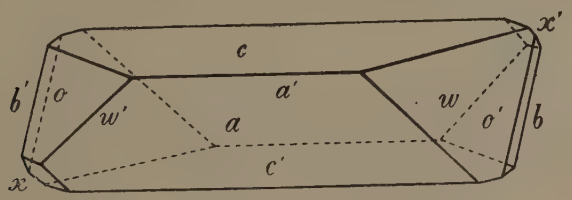


Fig. 9. *p-Toluene-sulpho-benzylamide.*

Triclinic-pinacoidal.

$a : b : c = 0{,}9778 : 1 : 0{,}8991.$

$A = 83°32'$. $\alpha = 83°24\frac{1}{2}'.$

$B = 90°56'$. $\beta = 91°33'.$

$C = 95°15$. $\gamma = 95°96'.$

Forms Observed: $a = \{100\}$, and $c = \{001\}$, large and very lustrous; in most cases a is somewhat larger than c; $\omega = \{111\}$ and $o = \{\bar{1}11\}$,

large, lustrous, and about equally well developed; $b = \{010\}$, narrow, somewhat dull, commonly with only a single face, often totally absent; $x = \{1\bar{1}\bar{1}\}$, small, dull, but well measurable. The aspect of the crystals is ordinarily prismatic parallel the b-axis.

Angular values:	*Observed:*	*Calculated:*
$a : c = (100) : (001) =$*	89° 4′	—
$c : o = (001) : (1\bar{1}1) =$*	47 33	—
$c : w = (001) : (111) =$*	55 47	—
$a : o = (100) : (111) =$*	59 4	—
$a : w = (100) : (111) =$*	51 12½	—
$o : w = (1\bar{1}1) : (111) =$	66 45½	66°50½′
$o : b = (1\bar{1}1) : (0\bar{1}0) =$	55 38½	55 46
$b : w = (010) : (111) =$	57 33½	57 23½
$x : a = (1\bar{1}\bar{1}) : (100) =$	57 38	57 38
$b : x = (0\bar{1}0) : (1\bar{1}\bar{1}) =$	62 50	62 42½
$o : x = (1\bar{1}1) : (1\bar{1}\bar{1}) =$	77 52	77 53
$x : c = (1\bar{1}\bar{1}) : (00\bar{1}) =$	54 24½′	54 34

No distinct cleavability was observed.

The extinction on a and c was oblique with respect to the edge $a : c$.

The specific weight of the crystals was: 1,313 at 17° C.; the equivalent-volume is thus: 198,78, and the topical parameters become: $\chi : \psi : \omega = 5{,}9793 : 6{,}1150 : 5{,}4981$.

§ 12. X. Nitro-p-Toluene-sulpho-benzylnitramide.

This compound, melting at 153° C., crystallizes from ethylacetate in small, very lustrous, colourless crystals. They often show somewhat oscillatory angular values; the faces of $\{001\}$ are, moreover, often curved. Exact measurements were, however, possible.

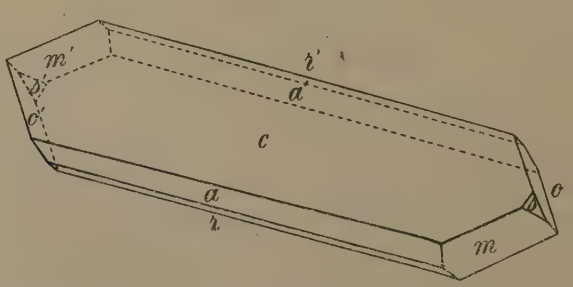


Fig. 10. *Nitro-p-Toluene-sulpho-benzylnitramide.*

Triclinic-pinacoidal.

$a : b : c = 1{,}8095 : 1 : 1{,}3139.$

$A = 95°34'$. $\alpha = 100°50'$

$B = 101°22'$. $\beta = 104°43'$

$C = 67°20'$. $\gamma = 65°33'.$

Forms Observed: $c = \{001\}$, large and lustrous, sometimes a little curved; $a = \{100\}$, narrower, but very lustrous; $m = \{110\}$ and $o = \{\bar{1}11\}$, almost equally well developed, and yielding good reflexes; $s = \{011\}$, small, but well measurable; this form is often absent. Further sometimes again: $r = \{\bar{1}01\}$, very narrow. The aspect of the crystals is tabular, thin plates parallel to c, and often elongated in the direction of the b-axis.

Angular values:	*Observed:*	*Calculated:*
$a : c = (100) : (001) =$	$78°38'$	—
$c : o = (001) : (\bar{1}11) =$	$62\ 28\frac{1}{2}$	—
$a : m = (100) : (110) =$	$79\ 13$	—
$c : m = (001) : (110) =$	$77\ 25$	—
$o : m = (\bar{1}11) : (110) =$	$54\ 10\frac{1}{2}$	—
$a : o = (\bar{1}00) : (1\bar{1}\bar{1}) =$	$56\ 48\frac{1}{2}$	$56°47'$
$o : s = (1\bar{1}\bar{1}) : (0\bar{1}\bar{1}) =$	$44\ 19\frac{1}{2}$	$44\ 10$
$s : a = (0\bar{1}\bar{1}) : (100) =$	$79\ 3$	$79\ 1\frac{3}{4}$
$a : r = (\bar{1}00) : (\bar{1}01) =$	$59\ 16$	$59\ 7$
$r : c = (\bar{1}01) : (001) =$	$42\ 6$	$42\ 15$
$s : c = (011) : (001) =$	—	$50\ 52$

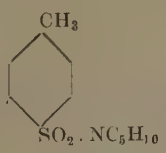
No distinct cleavage was observed.

On $\{001\}$ the extinction-angle is 8° with respect to the edge $a : c$. In convergent polarized light one hyperbola is visible at the border of the field.

The specific gravity of the crystals is: 1,530 at 17° C.; the equivalent-volume is therefore: 229,54, and the topical parameters are calculated at: $\chi : \psi : \omega = 8{,}6739 : 4{,}7934 : 6{,}2983$.

§ 13. XI. p-Toluene-sulpho-piperidide.

Structure:



This substance, which melts at 98° C., was obtained from ether in the form of large, flat, colourless, very lustrous crystals of rec-

tangular shape. They are well built, beautifully translucid, and allow very accurate measurements.

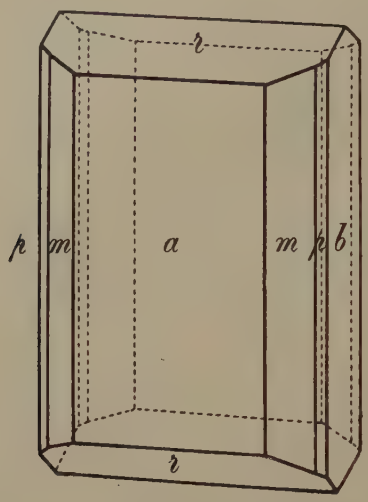


Fig. 11. *p-Toluene-sulpho-piperidide.*
Rhombic-bipyramidal
$a : b : c = 0{,}7474 : 1 : 0.3790.$

Forms Observed: $a = \{100\}$, predominant and yielding good reflexes; $m = \{110\}$ and $b = \{010\}$, large and very lustrous; $p = \{120\}$, very narrow; $r = \{101\}$, large and giving good reflexes.

Angular Values:	*Observed:*	*Calculated:*
$a : m = (100) : (110) =$	* 36°46½′	—
$a : r = (100) : (101) =$	* 63 6½	—
$m : p = (110) : (120) =$	19 23½	19°26½′
$p : b = (120) : (010) =$	33 50	33 47
$r : r = (101) : (\bar{1}01) =$	53 46½	53 46⅔

No distinct cleavage was found.

The optical axial plane is $\{001\}$, with the b-axis as first bisector; the dispersion, of rhombic character, is very appreciable: $\sigma < v$. The apparent axial angle is only small.

The specific weight of the crystals is: 1,281 at 15° C.; the equivalent-volume therefore: 186,57, and the topical axes become: $\chi : \psi : \omega = 6{,}5029 : 8{,}7005 : 3{,}2967$.

§ 14. XII. Nitro-p-Toluene-sulpho-piperidide.

The substance melts at 108° C., and crystallizes from ethylacetate in splendid large, somewhat pale yellowish, translucid, very lustrous crystals. They are well built, and allow good measurements.

Monoclinic-prismatic.

$a : b : c = 0{,}7466 : 1 : 1{,}5713.$

$\beta = 78°39'.$

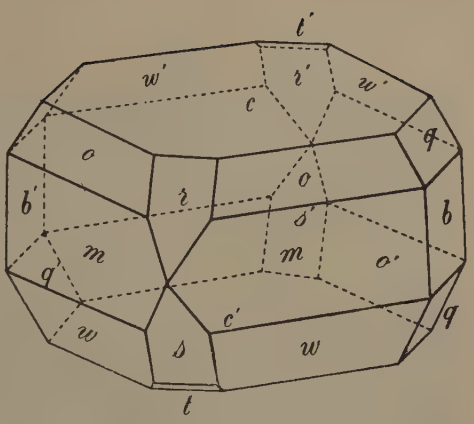


Fig. 12. *Nitro-p-Toluene sulpho-piperidide.*

Forms observed: $c = \{001\}$, predominant; $m = \{110\}$, large and lustrous, shows sometimes a fine striation parallel to the edges $m:c$; $o = \{\bar{1}11\}$, and $\omega = \{\bar{1}11\}$, about equally large, but a little bit narrower than m; $r = \{101\}$, well reflecting; $s = \{\bar{1}01\}$, somewhat smaller than r, often absent; $t = \{\bar{h}\,o\,k\}$, extremely narrow and not measurable only rarely present; $b = \{010\}$, small and narrow, dull; $q = \{011\}$ clearly developed, yielding good reflexes. The aspect is often isometrical, or somewhat flattened parallel to $\{001\}$.

Angular Values:	*Observed:*	*Calculated:*
$c:\omega = (001):(\bar{1}11) =$*	77°11′	—
$\omega:\omega = (\bar{1}11):(\bar{1}\bar{1}1) =$*	71 22½	—
$m:c = (110):(001) =$*	80 52	—
$c:r = (001):(101) =$	55 28	55°34⅔′
$r:s = (101):(10\bar{1}) =$	50 13½	50 16⅓
$s:c = (\bar{1}01):(001) =$	74 11	74 9
$c:q = (001):(011) =$	56 57	57 0⅔
$b:q = (010):(011) =$	33 3	32 59⅓
$\omega:s = (\bar{1}11):(\bar{1}01) =$	35 41	35 41¼
$m:m = (110):(1\bar{1}0) =$	72 22	72 24½
$c:o = (001):(111) =$	61 20	61 13⅓
$o:m = (111):(110) =$	19 30	19 8
$m:\omega = (110):(11\bar{1}) =$	21 57½	21 57
$m:b = (110):(010) =$	53 49	53 47¾

Very perfectly cleavable parallel to $\{001\}$, distinctly parallel to $\{110\}$. On $\{001\}$ diagonal extinction.

The specific weight of the crystals at 15° C. was: 1,384; the equivalent-volume is therefore: 205,20, and the topical parameters become: $\chi : \psi : \omega = 4{,}2031 : 5{,}6259 : 8{,}8455.$

Survey of the Crystallonomical Relations between the Derivatives of p-Toluene-sulpho-amide here investigated.

Name of the Compound:	Melting-point:	Symmetry:	Axial ratio:	Spec. Volume:	Topical parameters:
p-Toluene-sulpho-amide	137°,5 C.	Mon. prism.	1,2016 : 1 : 0,9364 $\beta = 87°29'$		
Nitro-*p*-toluene-sulpho-amide	141°	Mon. prism. (pseu o-rhomb.)	1, 2289 : 1 : 1,1812 $\beta = 90°$	133,99	5,5537 : 4,5194 : 5,3383
p-Toluene-sulpho-methylamide	76°	Rhomb. bipyr.	1,0358 : 1 : 2,6074	138,06	3,8442 : 3,7113 : 9,6770
Nitro-*p*-toluene-sulpho-methylamide	91°	Mon. prism.	1,0522 : 1 : 0,3948 $\beta = 86°40\frac{1}{2}'$	154,21	7,5664 : 7,1910 : 2,8390
p-Toluene-sulpho-methylnitramide	60°	Mon. prism.	1,3210 : 1 : 0,6892 $\beta = 78°6'$	165,06	7,5309 : 5,7009 : 3,9291
p-Toluene-sulpho-ethylamide	64°	Tricl. (pediaal)	0.6481 : 1 : 0.4136 $\alpha = 77°39'$; $\beta = 88°6'$; $\gamma = 102°55'$	152,26	4,6805 : 8,4202 : 3,4825
p-Toluene-sulpho-diethylamide	59°	Mon. prism.	1,0149 : 1 : 0,6762 $\beta = 72°1'$	184,55	6,6611 : 6,5633 : 4,4381
p-Toluene-sulpho-ethylnitramide	69°	Mon. prism.	1,0178 : 1 : 1,1005 $\beta = 88°11'$	168,27	5,4115 : 5,3169 : 5,8513
Nitro-*p*-Toluene-sulpho-ethylnitramide	76°	Mon. (sfenoïd.)	0,4812 : 1 : 0,8766 $\beta = 85°5'$	156,91	3,4652 : 7,2001 : 6,3119
p-Toluene-sulpho-benzylamide	113°	Tricl. pinac.	0,9778 : 1 : 0,8991 $\alpha = 83°24\frac{1}{2}'$; $\beta = 91°33'$; $\gamma = 95°26'$	198,78	5,9793 : 6,1150 : 5,4981
Nitro-*p*-toluene-sulpho-benzylnitramide	153°	Tricl. pinac.	1,8095 : 1 : 1,3139 $\alpha = 100°50'$; $\beta = 104°43'$; $\gamma = 65°33'$	229.54	8,6739 : 4,7934 : 6,2983
p-Toluene-sulpho-piperidide	98°	Rhomb. bipyr.	0,7474 : 1 : 0,3790	186,57	6,5029 : 8,7005 : 3,2976
Nitro-*p*-toluene-sulpho-piperidide	108°	Mon. prism.	0,7466 : 1 : 1.5713 $\beta = 78°39'$	205,20	4,2031 : 5,6295 : 8,8455

Groningen, June 1920.

Laboratory for Inorganic and Physical Chemistry of the University.

Zoology. "*The colour-markings on the body of Lepidoptera, compared to those of their larvae and pupae, and to those of their wings*". By Prof. J. F. VAN BEMMELEN.

(Communicated at the meeting of January 31, 1920).

In former communications I have expressed my conviction, that originally an intimate connection must have existed between the colour-markings of caterpillar, pupa and butterfly of the same species, all three being only varieties of one and the same archaic form. Consequently the few cases, in which this connection is evident at first sight, should not be considered as mere casualities, but as resulting from the preservation of the primitive condition. SCHIERBEEK, who chiefly studied the setal pattern of the youngest instars of caterpillars, but also gave his attention to the colour-markings of a few older caterpillars, and to pupae, has fully corroborated my views. DE MEYERE on the contrary, in his paper: Zur Zeichnung des Insecten-im besonderen des Dipteren- und Lepidopterenflügels, 1916, has expressed his doubts about them, where he says on p. 131: "In my opinion the striking difference between the pupal- and the imaginal markings precisely shows that they have had an independent origin, and have followed different ways: — just as we found it in nearly related Diptera, we here see it in different stages of the same animal".

And further on:

"According to my view the colour-markings of the pupa of diurnal Lepidoptera are as much of recent origin as their frequently grotesque shape and their very varying mode of fixation. The same might apply to pupal markings in comparison to those of caterpillars".

In his second paper: Zur Evolution der Zeichnung bei den holometabolen Insecten, he writes on p. 70:

"I consider the striking colour-markings of many butterfly-pupae as a secondary feature in these organisms, exposed to light as they are. In a similar manner the pupa of *Abraxas grossulariata*, which settles unhidden in shrubs, shows special coloration. VAN BEMMELEN's assertion, that this Geometrid should show a primitive coloration in all instars, does not seem right to me, at least in regard to the pupa . . . . The pupa of *Abr. sylvata*, which hibernates in the earth, is quite dark; without doubt in this case, the older condition. The real primitive condition I believe to occur in the light-brown

pupae of many Micro's, of Hepialids, Limacodids etc., all these being very like the pupae of Neuroptera".

As I already pointed out in my paper on the primary character of the Pupal pattern in Butterflies (Proc. K. Akademie van Wetenschappen 1918) I feel justified in fully maintaining my views.

I now wish to discuss somewhat in detail, a few examples of similarity between larva, pupa and imago, chosen from the family of Sphingids. It is true that up till now I have not been able to investigate the subject in full, as I have not yet got acquainted with the younger larval instars by personal inspection, nor found occasion to study the development of the colour-pattern inside the pupal sheath. The comparison of the markings in some nearly-interrelated species of caterpillars in a full-grown state, as well amongst themselves as with those of their imagines, and in a few cases also with marked pupae, gives us such a number of striking proofs of original unity, that I consider my assertion satisfactorily backed by evidence. I therefore believe it worth-while to direct the attention of entomologists to this highly promising subject, especially so, because a complete insight into the course of evolution of the larval, nymphal and imaginal colour-patterns of a tolerably vast number of species can only be obtained by cooperation of a great many competent investigators.

From times remote the wing-markings of butterflies have attracted the curiosity and admiration of men, but to those of the body proper only in exceptional cases a little attention has been given, and then still from a purily descriptive point of view. Intercomparison of the colour-markings on the bodies of related species, or investigation of the similarity between the design on the body and that on the wings has hardly ever been tried; only when a striking resemblance between the two latter exists, is this sometimes made mention of, but only as a casual remark.

Yet it is evident, that when comparing the imago with its caterpillar, only the markings of the body need be minded, and that the same applies to the pupa, though in a minor degree, as in the latter only the upperside of the forewing is exposed to view, while on the contrary part of the lateral body-wall is hidden beneath the wing-sheath.

When moreover we wish to study the connections between the markings on the wings and those on the body, it seems desirable first to realise the exact nature of the wings. Now these organs may be considered as lateral folds of the dorsal skin of the meso- and metathorax, near to and dorsally of the line of stigmata (though these openings are obliterated in the said segments of the thorax). Consequently each wing consists of a dorsal and a ventral lamella of

the skin, which along the wing-border fold over into each other. When we imagine this fold to become repressed up to the first initial rudiment of its evolution, then these lamellae do not extend horizontally along parallel planes in contact with each other, but quite the contrary lie in one and the same dorsoventral plane. When in applying this mode of representation of the wing we look at it from the side, it is seen projected on the lateral body-wall, and so each wing can be drawn as a sexangle, which by its horizontal diagonal is divided into a dorsal half (the upper wing-surface) and a ventral one (the underside of the wing): the diagonal itself representing the wing-border. That by this projection-method the wing-field appears extremely small in relation to the dimensions of the body, need not according to my view be considered as a real objection against it. For the relation in size between wings and body in different species of Lepidoptera varies between very wide limits, and in the females provided with rudimentary wings of sundry species it even approaches the schematic condition described. Likewise during the pupal stage of almost all kinds of Lepidoptera the wings are far smaller than after the emersion from the nymphal sheath.

This projection of both wing-surfaces upon the dorso-ventral plane sharply draws our attention to the fact that markings, which on the wall of the body stretch in an oro-aboral direction, will run in a so-called transversal one over the wing-surface, i. e. from the anterior towards the posterior wing-border. The dorso-ventral components of the pattern on the contrary will traverse the wing-field from root to external margin (commonly called longitudinally). In the same way this method can give support to the belief, that the pattern of the upper surface need not originally have been identical with that of the underside, as they correspond to different, though neighbouring areas of the sidewall of the body.

Finally this way of representing the wings as projected on the body highly facilitates and accentuates the comparison with the caterpillar. To get a pure comparison with the pupa however, we are obliged somewhat to modify the position and the size of the sheath of the forewing, which involves the formation of an empty space towards the side of the abdomen, corresponding to the place where the hind-wing would have been situated, when this were visible on the pupa.

In order to insert the real wing-pattern into these schematic sexangles, we have to project it upon them. To do this, we must turn the wing obliquely up- or downwards and draw a contracted image of its colour-pattern on the perpendicular plane of projection.

Moreover it is desirable to apply this same method of projection to the dorsal and ventral body-wall, in such a sense that the circumference of the figure no longer corresponds to that of the sideview of the animal, but roughly forms a trapezium, the upper- and underside of which represent the median dorsal and ventral lines, or better still, stretch a little over them. This can also be expressed in such a way, that the body becomes compressed from left to right, thereby growing higher in the dorsoventral direction, a condition so often shown in reality by squeezed specimens. As to the position of the wing-sexangles in regard to each other, I am of opinion that they should be placed in one and the same horizontal body-axis, the one behind the other, instead of the anterior margin of the hindwing passing beneath the posterior one of the forewing. In size the two wings may be represented alike. The arguments for both these assumptions can be found in the wings of Hepialids.

Consecutively the following points should be attended to in the investigation:

a. comparison of the markings of the thoracal with those of the abdominal rings in one and the same individual, therefore in the caterpillar with its different instars, in the pupa, and in the imago.

b. comparison of the colour-pattern of all these stages, to each other in the same species.

c. comparison of kindred species in their successive stages with each other.

For each of these comparisons an example may be given.

Of the few Sphingid-caterpillars which were at my disposition, I choose the fullgrown larva of *Protoparce convolvuli* (scil. the brown variety) as a fit object for comparison of thoracal with abdominal markings. For in this species the relation of the one to the other can be very clearly observed, and in doing so, we are impressed by the fact that the first seem to bear a more primitive character than the second. For on the thorax the obliquely ascending lateral bars, which are so characteristic of the abdominal segments of these as of so many other Sphingid caterpillars, are absent. The pattern is restricted to longitudinal light and dark stripes, which in their turn are evidently composed of rows of spots, whose number corresponds to that of the annuli or secondary rings, which enter into the composition of each body-segment of the caterpillar. The number of these annuli is constant, eight for each segment of the abdomen, except the posterior two; it is likewise diminished in the thoracal ones, probably an effect of reduction. On each annulus one row of light spots on a dark ground is seen. The relative size of the single

spots determines the impression they call forth, either of a light or of a dark party of the caterpillar-skin. While light spots on the same level on successive annuli arrange themselves to light longitudinal stripes, small spots on the contrary appear as light specks in a dark band. Here and there these specks totally vanish, a larger black spot being the result. So the prothorax shows no other ornamentation than a pair of big epistigmal dark blotches on its flanks, passing in a caudal direction into the dark longitudinal strokes, which on the abdominal segments periodically become transected by the oblique light stripes. On meso- and metathorax a light brownish-yellow median dorsal stripe is present, flanked at some distance by light subdorsal stripes, separated from the firstnamed by dark bands, which in the anterior part of each segment bear the character of dark spots.

Beneath the line of the stigmata runs a very broad light streak, over the roots of the legs two dark longitudinal lines are seen.

All these markings are found again on the abdominal segments, but in a modified, more complicated condition. The dorsal stripe passes uninterruptedly from thorax to abdomen in the form of a light band, slightly contracting in the middle of each segment, while at its anterior margin a pair of yellowish-white spots, separated by a small dark stripe, contribute to render the first annulus of each abdominal segment more conspicuous. But in the first place this effect is reached by the two sharply drawn brownish-black spots at the lateral side of the just-mentioned light dorsal maculae, and by the clear white specks, which in their turn flank the outer side of these maculae.

This series of alternately light and dark spots on the first annulus evidently only consists of nothing more than highly conspicuous links in the prolongation of the above mentioned three light and two dark lines that run over the dorsal side of the thoracal segment. It is therefore in harmony with this fact, when we remark that from each of the black blocks a dark streak runs on in a caudal direction. These streaks converge towards the centre of the segment, in harmony with the median light dorsal streak, which narrows in the middle of each abdominal ring, while towards the back end of the segment the streaks again diverge. Consequently the dorsal stria broadens towards the latter margin and so forms a triangular area, which somehow assumes the character of an independent spot; this aspect being heightened by the repetition, in the centre of the segment, of the small black stripe in the middle line on the first annulus.

Looking from the lateral side, the similarity between thoracal and abdominal designs likewise strikes us, but at the same time we remark the deviation of the latter from the original condition, in

consequence of the differentiation of the oblique light stripes which ascend in a dorso-caudal direction, and are accompanied along their dorsal border by an obscuration of the brown-black ground-colour (called "dunkle Grundierung" by v. Voss). At their posterior top these oblique light stripes exactly pass into the above-mentioned white subdorsal spots, in the same way as their accompanying dark seams join the black specks, which themselves run on into the dark subdorsal lines. A similar broadening and obscuration of the seam, as is caused by these specks at the dorsal end of the oblique stripes, is also found at their ventral beginning, on the level of the stigma. The latter however is situated at the back side of the light oblique stria (on the suture between the 3 and 4 annulus), while the mentioned dark spot lies before it on the 2 annulus. Still further forward to the front side, the corresponding part of the first annulus also bears a pair of dark maculae (praestigmal spots). The stigma itself is likewise coloured dark. In advance of the stigma the dark diagonal stria is still continued in a ventral direction over the posterior four annuli of the foregoing segment, and reaches the ventral border of the broad light substigmal band, where it joins the horizontal undulating line over the base of the false legs.

Now in this brown variety of *convolvuli* we see at once that all these spots and stripes are nothing else but more or less differentiated parts of the general ground-pattern, which exclusively consists of rows of light maculae on a dark ground, keeping rigorously to the annuli, and therefore repeated eight times on the succeeding abdominal segments. In each row the number of maculae is large, yet tolerably constant, viz. ± 13 at either side of the median line.

The above described black spots are formed by the blending of dark stripes separating the white specks, the light blotches on the contrary by the obliteration of one or more of these stripes.

Likewise the light diagonal stripes are built up by an obliquely rising series of eight light maculae that have increased a little in size, the dark seam in the same way by a similar gradation of black cubes, lying dorsally to these light maculae.

Comparing the brown with the green variety, we remark that the latter has got nothing left of the entire ground-pattern but the larger dark maculae: the subdorsal, the epistigmal, the prostigmal, the stigmal and the hypostigmal or the basal spot. Of these the epistigmal spot still betrays its original character as a part of the dark seam along the diagonal stria by its obliquely extended shape in a dorso-caudal direction, pointing so to say to the subdorsal stripe of the following segment.

On the metathorax of the green variety the subdorsal spots are present in double number, on the metathorax in single.

Comparing the larval design to that of the imago, we may here remark in parentheses, that the last-mentioned pair of spots also occurs on the caterpillar of *atropos* and here maintains itself as the eye-spots of the cranium-image.

The collection KALLENBACH also contains a halfgrown *convolvuli*-caterpillar, I therefore found occasion to compare this with the fullgrown larva, and thus could convince myself that the light subdorsal maculae of the latter really are the remnants of a complete subdorsal line, originally stretching over the whole series of the body-segments, in the same way as the substigmal line. On the abdominal segments however it is periodically broken by the diagonal striae which, though rather inconspicuous, are yet present in complete order, and which, before each stigma, meet the segments of the substigmal line, thereby forming a triangular spot on each body-ring. But the chief difference between this halfgrown caterpillar and the fullgrown one is its uniform dark ground-colour, sharply contrasting with numerous small white oval knobs, which stand arranged in several rows on the eight annuli. On the above-mentioned light longitudinal lines these knobs occur in the same way. They do not make the impression of standing in any relation either to the dark or to the light specks, their own hue in fact is a much clearer white than that of the latter. So we can only suppose, that at the last moult they disappear, to be replaced by the (tolerably regular) white spots in the dark ground-colour.

When we pass from the caterpillar of *convolvuli* to that of *atropos* and *ligustri*, the design of these latter two is seen to correspond to that of the first in all such instances, as can be considered as secondary modifications of the original pattern; those parts of it on the contrary, which in *convolvuli* are found in the least modified condition, having nearly vanished in the other two species. The same may be said of the thorax: here the process has led to total absence of pattern in *atropos* and *ligustri*. Upon the abdominal segments on the contrary the pattern is the same for all three, only differing in shades and in completeness.

These facts undoubtedly offer new and valuable arguments for the supposition, that the absence of pattern is a consequence of obliteration; the two latter species therefore having suffered stronger regression from the original condition than *convolvuli*.

Still in another instance the lastnamed species seems to show the more primitive conditions, viz. in the simple and few colours that

enter into the composition of the pattern: darkbrown and diluted yellow. It is true that these colours only maintain themselves in the older instars of the larval period, as originally the caterpillar is green. So when we should ascribe a general applicability to the rule that the colours and markings of the younger stages invariably represent more original conditions than those of the later, we should be obliged to suppose that the brown colour had arisen from the green one. But though this rule can be applied in many cases, it by no means may be considered as of universal validity. Especially in insects I am of opinion that everywhere the green colour is a secondary modification of other shades, which lie farther to the red side of the spectrum, as I have already tried to demonstrate in my paper on the genus Charagia among Hepialids.

In *convolvuli* therefore the change from green to brown should be considered as a reversion to more primitive conditions, and in connection with this supposition we might regard the green colour in *ligustri*, and to a certain extent also in *atropos*, as due to secondary modification [1]). Possibly this change in the general shade might be brought in connection with the reduction of the original design, which on the thorax has led to complete, on the abdomen to partial obliteration, and moreover on the latter has called forth a greater contrast between the uniformised green ground-colour and the very obvious pink and white oblique striae.

As a hint that in *convolvuli* the brown caterpillar has best retained the original character, we may also regard, that in this species the connection of the markings with the everywhere occurring subdivision of the body-segments in a series of eight annuli or subsegments is most conspicuous. But likewise in the other two species it is obvious that the diagonal striae (pink and white in *ligustri*, pink and yellow in *atropos*) are composed of a step-like series of dark and light blocks of colour. With regard to this feature, those of the firstmentioned species strike us by the peculiarity, that in the forward prolongation of the diagonal striae on the foregoing segment a row of three or four white specks occurs, growing smaller from behind forward. In this anterior prolongation of the white striae the blending of the specks, which enter into their composition, has not yet taken place.

In the green caterpillar of *atropos* another proof is seen for the assertion, that more extensive striae, bands and fields of colour are the result of the blending of smaller spots arranged in transverse rows. For

[1]) This species also possesses a brown variety of the caterpillar, and this, as well as that of *convolvuli*, shows a more complete and primitive pattern than the green one.

on the bluish dorsal stripe as well as on the neighbouring yellow subdorsal bands and the pink-red oblique lateral bands, we find groups of knobs, which evidently are regularly arranged on both sides of the median line, in eight transverse rows, which correspond to the annuli composing each segment, the number of the wharts in the blue diminishing from before backwards in the ratio of three to two to one. Each knob carries a hair, or at least was originally provided with one. On the pink bands the knobs have the same hue as the band itself, only a little deeper, in the yellow and the blue on the contrary they retain that same pink colour of their own. On the anterior row of each segment, where the number of wharts in the blue reaches its maximum (3 or 4 at each side of the median line) the wine-red colour even extends around the two lateral tubercles, and embraces them in one larger deep-red blotch. Surveying the whole of the segments, these blotches are seen arranged to both sides of the median line in a series marking the subdorsal line; this series can be retraced in *convolvuli*, in the form of the rows of dark subdorsal spots described before, which rows are in immediate contact with similar ranges of clear yellow-white maculae, nearer to the dorsal line, the latter itself being marked by dark stripes (3, one behind the other, on each segment).

When now we pass to the survey of the body-markings of the imagines and begin with the abdominal segments of *convolvuli*, we here again meet the dorsal line as a series of little black stripes. To both sides of this the subdorsal design is arranged as a sequence of grey areas touching the dorso-lateral colour-markings with a special convexly-curved borderline. These fields themselves are composed on each abdominal ring of three transverse bands: a narrow anterior one of white, and two much broader ones behind, the first pink, the second jet-black. This set of three transverse bands is repeated seven times: at the end comes one segment with only a black dorsal stripe. The ventral border of this lateral pattern forms an almost straight line, situated at a certain distance above the row of stigmata. The intervening epistigmal seam is coloured less conspicuously in the same way as the entire hypostigmal ventral surface; yet it is possible to distinguish darker sets of hairbundles, which associate with the red and black bands, and a row of white bushes of hair stretching right above the stigmata.

Though as mentioned, the ventral side shows no vividly coloured pattern, this uniformity of hue is precisely the cause, that a set of two dark spots in the ventral middleline, at the front-border of the fourth and the fifth abdominal segment, is highly conspicuous.

In my opinion the transverse markings of the dorsolateral fields might be ascribed to the original distribution of the colour in dorso-ventral bars, corresponding to the eight annuli which enter into the composition of each segment; probably the white represents the first annulus, the pink area the following four, the black the posterior three, but in *convolvuli* the limits of the single rings are indistinct. As we shall see, this division can really be traced in imagines of other Sphingids.

Now comparing this pattern of the abdomen to that of the thorax, we remark that the grey ground-colour along the dorsal side of the latter, provided with three darker longitudinal striae on both sides of the middle-line, evidently may be considered as a broadening of the dorsal markings of the abdomen. Over the root of the wings runs a greyish-white streak of long, soft hairs, forming a continuation of the white transversal markings of the abdominal segments, especially of their dorsal part, which on the second segment already has the shape of an isolated round white blotch. This light stripe over the wing-root (epipterygial stripe) should probably not be considered the homologon of the white subdorsal line on the thorax of the caterpillar.

In the third place an evident connection exists between the markings on the upperside of the hindwing and those on the dorsal side of the body, as well of the thorax as of the abdomen. The said wing-design consists of dark spots arranged in bands on a lighter ground. These bands apparently stand perpendicularly to the longitudinal axis of the body, thereby agreeing in position with the anterior three black transversal rings on the abdomen. As a matter of fact however they are not transverse but longitudinal bands, because they run from the anterior towards the posterior border of the wing, the apparent transverse position only being a consequence of the rounding off and reduction of the hindwings, which in Sphingids has taken place in an extreme degree.

When as described before, the hindwings are projected upon the lateral walls of the thorax, the dark bands may be drawn on the wing-fields as *longitudinal* lines, viz: in an oro-caudal direction. In this way the similarity with the lateral design of the abdomen, which at first aspect is so striking, withdraws to the background, or, rather, is reduced to its real proportions.

Indeed, as well as the design on the annuli of the thoracal segments of the *convolvuli*-caterpillar, that on the wings is seen to consist of dorso-ventral rows of alternately dark and light spots, which are arranged in longitudinal chains, by their situation at the same level

upon the succeeding annuli. It is true that the surface of the wing is not divided into regular annuli in the same way as the body-wall, yet also its surface becomes parcelled into so-called cells by means of the venous system, this division showing a considerable amount of similarity to the first-mentioned division in annuli. One even might feel tempted to ascribe a certain importance to the fact, that in the neighbourhood of the wing-root the number of internervural cells is equivalent to that of the annuli of the larval segments, when the original number of veins in the proximal area of the wing is taken to be eight, (costa, subcosta, radius, medius, cubitus and three anals).

Comparing the body-design of the *convolvuli*-imago to that of the corresponding stages of *ligustri* and *atropos*, the similarity is obvious on first view, and not less striking than that of the wing-patterns. But entering into details, which at first sight might seem to be trifles without deeper meaning, a few curious features may be remarked, which draw the original similarity with the caterpillars into stronger evidence. So in *ligustri* the contrast between the light areas on both sides of the black median dorsal line and the enlarged dorsal tops of the black transversal bars, is sharper than in *convolvuli*, these broadened black tops, protracted as they are towards the head-side, producing the impression of a sequence of dark subdorsal spots separated by the lateral emergencies of the front-corners of the lightbrown subdorsal fields, in a higher degree than is the case in the lastnamed species.

Likewise in *ligustri* the white lateral transversal stripes along the frontborder of the segments are lacking, or to express it more correctly, the white is replaced by black, which coalesces with that along the back-border of the foregoing segment, the black between the first and the second abdominal segment being restricted to a subdorsal blotch. Moreover the ventral ends of the black and of the red transversal bands are obliquely truncated, which calls forth the impression of a zig-zag-line, running at a certain distance above the series of the stigmata, which line corresponds to the system of diagonal stripes on the abdominal segments of the caterpillar.

At the ventral side the design has remained unaltered in a much higher degree than in *convolvuli*, the dark ventral line stretching over the whole of the segments. At both sides of this line light areas are found, which at the level of the stigmata are marked off by a dark festooned line. On the thorax the resemblance with *convolvuli* is striking, and especially the light epipterygial band is drawn with peculiar sharpness.

The similarity in design between the abdominal segments and the hindwings is still more obvious than is the case with *convolvuli*,

because in *ligustri* the groundcolour of the hindwings plays into a rose-red hue, especially in the neighbourhood of the wing-root, this red even running over into the root of the forewings. The black wingbands lie more exactly in the prolongation of those of the anterior abdominal segments and show fewer traces of their origin by the coalescence of a row of intervenous spots.

All the above-mentioned resemblances are equally found in *atropos*, only the hues and the variegations being different. When we start from the abdomen, the dorsal stripe on its back corresponds to that of the caterpillar as well in the V-shape of its segments as in its blue shade. The rose-red colour of *convolvuli* and *ligustri* is replaced by stark-yellow and the dorsal borderlines between the yellow lateral areas on the abdomen and the blue dorsal patches run in the same oblique direction as the lateral sides of the V-shaped elements of the dorsal design in the caterpillar. At the ventral side of the abdomen the black design along the frontborder of the segments, at least of the anterior ones, is well developed, and shows well-marked enlargements along the hypostigmal and subventral lines, pointing to the presence of series of spots at those levels.

As well as in *ligustri* the light (in *atropos* yellow) hue of the lateral walls of the metathorax is continued not only on the hindwings, but also on the root of the forewings, though it does not reach the front-margin of these latter.

The cranial design on the dorsal side of meso- and metathorax may be easily traced back to sets of dark spots on a light ground: two pairs of these spots standing on the meta-, one on the mesothorax, just as is found in the caterpillar, and in the same way in the imagines of many other Sphingids as well as in those of other Heterocerous families. The contour of the skull-image corresponds to the dorsal or medial dark longitudinal thoracal line, which forms the borderline of the median area of the thorax, in the same way as in *convolvuli* and *ligustri*. The more ventral or lateral thoracal-line is likewise present in *atropos*, and next to it also the epipterygial light streak, though here this latter does not show the grey shade of *convolvuli* or the white of *ligustri*; but a dark bluish grey, which of course renders it much less conspicuous.

Lastly comparing the three stages of *Chaerocampa celerio*, as well with each other as with the corresponding stages of the three above-mentioned Sphingids, we meet again with all the already remarked peculiarities, but here they are in some regards more complete and better pronounced, in other points more original, in still other on the contrary more modified, either in a higher degree or in a different way.

E.g. in the fullgrown caterpillar the contrast between thorax and abdomen is of the same nature and as strikingly pronounced as in that of *convolvuli*. The dorsal stripe is only marked by a thin but sharply drawn black line, extending all along the thorax, but on the abdomen only covering the anterior three segments. The light subdorsal and epistigmal lines on the contrary are well developed on the thoracal segments, the first runs up to the big ocellus-spot on the first abdominal ring, this spot, as WEISMANN's investigations have proved, differentiating itself in the course of development of the caterpillar from the anterior part of the subdorsal line on this segment, while at the same time the posterior part obliterates.

The second eye-spot is formed in the same way. In the specimen at my disposal this spot was much bigger and more purely circular at the left side of the body than at the right. On the latter side however the spot consisted of two parts, lying immediately behind each other, and so betrayed its real nature as a part of the subdorsal line still better than at the opposite side.

On the next abdominal segment traces of the light subdorsal line can still be detected, and likewise of dark spots immediately above it on the level of the first annulus. Above the stigmata of the abdomen dark diagonal striae run upward, bordered at their ventral side by light stripes: proving that the common motive of design of the Sphingid caterpillars is present also here. These striae and stripes, though occupying the whole length of the segments, yet figuratively speaking seem to be drawn on a back-ground of light spots and dark stripes, which themselves are strictly bound to the division of the segments into annuli.

Moreover a contrast exists between the dorsal and the ventral side. On the first we meet at every annulus with a row of small black stripes, between which the ground-colour is lighter and therefore makes the impression of clear spots separated by black lines. This part of the design shows a great similarity with the annuli-markings of the full-grown *convolvuli*-caterpillar.

At the ventral side on the contrary each annulus carries a row of white lentiform knobs, constituting the basal cushions of short setae. On the level of the epistigmal area the knobs pass into the light spots, evidently the latter occupy the same place as the former, at least the knobs diminish in size and conspicuousness towards the dorsal side. This feature therefore confirms the assertion that the colour-pattern of the fullgrown *convolvuli*-caterpillar may be derived from the condition before the last ecdysis, by supposing the knobs to fall out and to become replaced by the light spots. It also deserves

attention, that in *celerio* the knobs have maintained themselves at the ventral side of the caterpillar, in *atropos* on the contrary at the dorsal surface, while in *ligustri* they are totally absent, probably an effect of obliteration.

These rows of knobs, standing regularly arranged along the annuli, probably represent the same feature as the chagrination of the larval skin, mentioned for many Sphingid-caterpillars by Weismann and Voss, these investigators however having paid no special attention to this feature. When studying the figures, which the latter author gives for the younger instars of the Smerinthus-caterpillars e.g. the yellowish-green variety of *S. ocellatus*, (fig. 22, III stage and 23, III stage), we find distinct indications of these light spots arranged in a dorso-ventral row on the annuli. Judging from older figures of *Ceratoma amyntor* and *Pogocolon nessus*, the rows of setiferous knobs here run regularly from the dorsal to the ventral side of all the segments, those of the thorax as well as those of the abdomen.

Now comparing the caterpillar of *celerio* with the body of the moth, the correspondence in design in many regards is still more striking than in the before-mentioned species of Sphingids. For on the dorsal side of the abdomen of the imago the markings consist of alternating light and dark longitudinal lines, and these lines are seen to be composed of a chain of coloured patches, which on every segment clearly show the division into annuli, just as on the body of the caterpillar. On the first and the last annulus of each segment the design is developed best: silvery-white spots in the dorsal median line and subdorsal stripes marking the anterior and the posterior border of the anterior abdominal segments. Along either side of the median line (which behind the mentioned white spot carries a series of black stripes), dark bands run in a longitudinal direction; these as well as the median stripe are prolonged over the thorax. To the lateral side of these three dark bands a silvery stripe is formed, the homologue of the subdorsal line, and over the root of the wing we again meet the light epipterygial stripe which runs on to the head above the eye, and shows a great similarity to the epistigmal stripe of the caterpillar. But on the abdominal segments we are likewise able to distinguish stigmal, hypostigmal, subventral and ventral longitudinal bands, and we also see that the epistigmal, the subdorsal and the dorsal bands are characterized by the occurrence of silvery-white bushes of hairs. Using a magnifying glass for more minute observation, each of these stripes is seen to be again composed of lighter and darker bushes and groups of specks, the whole circumference from the dorsal to the ventral median line therefore

showing no less than 27 colour-patches varying in hue. E.g. the brownish-black bands to either side of the dorsal median stripe are by no means uniformly coloured, but show a mosaic of black and light scales. These bands pass on to the thorax almost unmodified. Especially the continuation of the subdorsal stripe on the thorax is striking, as the white bushes, which characterize this stripe on the abdomen, are also seen on the thorax. The epipterygial stripe evidently represents the prolongation of the epistigmal line, this line being likewise marked by yellowish-white bushes. Behind the eye the subdorsal and the epipterygial stripe unite into one.

But traces of the diagonal stripes may, I believe, also be detected, at least in some specimens, in the shape of dark and light oblique bands on the sides of each segment, above the stigma. Those features which in *celerio* are either absent or very indistinct, are unmistakably present in other species, e. g. *alecto*. About the wing-design of *celerio* we still want to remark that the considerable difference between the upper surface of the fore- and that of the hind-wing, in contrast to the nearly perfect similarity of both wings at their underside, probably points to the fact, that the upperside has become secondarily modified to an important degree. Now it is remarkable that at this side the forewings, in hues as well as in design, show greater similarity to the dorsal side of the thorax and abdomen than does the hindwing, notwithstanding the fact that on the first-named the *V*-diagonal design (as I have called it) is strongly expressed. Moreover this design, with regard to the direction of the diagonal-line, possesses a striking similarity to the oblique markings on the abdominal rings of the caterpillar. This similarity especially enters into evidence, when the wing is projected in the above-described way on the lateral wall of the thorax.

In conclusion I wish to say a few words about the design of the pupae, which in Sphingids, as already mentioned in a foregoing paper, has been preserved more or less, especially in the group of the Chaerocampinae. It consists of dark blotches on a lighter ground: shape and size of these blotches is rather irregular, yet it is clear that they are arranged in rows, corresponding to the dorsal, subdorsal, epistigmal, stigmal, hypostigmal, subventral and ventral lines of the caterpillars and imagines. In a few specimens, which I found occasion to investigate (amongst which was one of unknown derivation, the species therefore remaining uncertain to me) the number of these rows of spots is much higher, which leads to a striking resemblance with the design of imagines, especially *celerio*. Though I could not yet find leisure to study in details the similarity between caterpillar

and imago (eventually also pupa) of other forms than the Sphingids, I feel convinced, that it may be proved for a great many Lepidoptera, e.g. Saturnidae and many Bombycidae, and certainly also for Geometridae.

From the above mentioned observations I feel justified in making the following deductions:

The markings on the body of caterpillars, pupae and imagines follow the same rule as those on the wings of the latter. Consequently the original design is regular, simple, limited to each segment separately, complete, uniform over the whole extent of the segment, bound to the dispersal of the setae over its surface, and to the division of the latter into secondary rings or annuli. The colour, in which this pattern is executed, may differ, and is of no account as to its real character. Yet there exists a certain connection between different hues: green for instance always appearing as a secondary modification of other shades, especially brown, grey or yellow.

Modifications of the original pattern take place in a similar way and after the same rules as those on the wings. Through the accentuation of a contrast in shades between neighbouring spots, which originally were similarly coloured, a richer gamma of hues may be produced. Vertical, horizontal and oblique lines are formed by coalescence of rows of primary spots; maculae, eye-spots, bands and areas result from the accrescence of spots and (or) their blending with others in their vicinity. Finally the whole bulk of the separate spots may merge into one general shade.

Attention should also be paid to the fact, that in the same way as the front-seam of both wings is often marked in a different and stronger way than the rest of the surface (especially at the underside), the first annulus of each segment likewise surpasses the rest of the annuli in sharpness of design and coloration.

However restricted the material for my investigations may have been, it has convinced me still more of the validity of my assumption, that a primary relation exists between the colour-design of caterpillar, pupa and imago, the pattern of the imaginal instar often showing a more primitive type than that of the fullgrown caterpillar.

The contrast between thoracal and abdominal pattern, which already in the younger instars of the caterpillar manifests itself in the different distribution of the setae (comp. J. T. Oudemans and A. Schierbeek), maintains itself as well in the later instars by differences in colour and design, occurring in the great majority of caterpillars. An identical design on thorax and abdomen is probably the result of secondary change.

Groningen, January 1920.

Physics. — *"On Centres of Luminescence and Variations of the Gas Pressure in Spectrum Tubes at Electrical Discharges."* By L. HAMBURGER. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of April 23, 1920).

1. *Introduction.*

Three years ago [1]) we published the results of some observations, in which among others the fact was stated that when discharges are sent through a spectrum tube, variations of the gas pressure may occur at the anode and the cathode.

They owe their existence to the difference in properties of positive and negative ions. As J. STARK [2]) already observed, the difference existing between the two kinds of ions gives rise to the two following effects:

a. The appearance of phenomena connected with the electrical wind (in general the electrostriction).

b. Mass transportation by means of the electric current.

The object of this paper is among other things to examine which of these two effects, which are in connection with each other, as they both rest on the difference in properties of the ions, has a greater part in the observed variations of the gas pressure. In connection with this the centres of electro-luminescence will then be considered.

2. *Electrostriction.*

A Dutch physicist D. BOS [3]) has already made an extensive study of this. He finds for gases such slight variations of volume, resp. of pressure, (loc. cit. p. 92 et seq.), that it is clear that with the pressure effects observed by us — to an amount of 30 % and more of the total pressure — electrostriction cannot have had an appreciable direct influence.

In the case of discharges through a spectrum tube the phenomena of the electrical wind connected with electrostriction may be considered as a consequence of the friction between the ions and the neutral gas molecules. It is clear that the electrical pressure will be the greater as the difference in properties of the positive and negative ions is greater. As we already mentioned, this electrical pressure is of an entirely different order of magnitude than the variations of the gas pressure observed by us.

[1]) L. HAMBURGER, Diss. Delft 1917. These Proc. **20**, 1045 (1917).
[2]) J. STARK. BOLTZMANN-Festschrift 1904.
[3]) Diss. Groningen 1880.

3. *Mass Transportation by means of the Electric Current.*

The discharge of the ions taking place at the electrodes, however, gives rise to a state which may be considered as an accumulation of what was discussed before.

To the existing difference in properties of the oppositely charged ions corresponds to a certain extent the difference between the gas molecules formed from them by the discharge at the electrodes. Though the direct influence of the difference of the ions on the gas pressure is slight, the influence on the gas pressure assumes quite different proportions when it is kept in view that *constantly* the electrically charged particles withdraw from the ion-conditions. Resting on the same primary basis as the electrical wind, this accumulation leads to the effect that manifests itself much more strongly: *mass-transportation by means of the electric current.*

In general on discharge of the ions taking place at the electrodes, another number of gas molecules will be liberated at the cathode than at the anode.

In consequence of this a constantly increasing difference of pressure would be found in the two parts of the tube, if not another counteracting effect made itself felt. It is, indeed, clear that, when a difference in pressure occurs through the application of the electric field, the gas molecules will oppose this, and try to annihilate the difference in pressure by diffusion in the opposite sense. The resulting difference of pressure then corresponds to a stationary state, in which an equal number of molecules are brought back to the path of the current through diffusion, as new ones — in ion-form — are conducted to the electrodes by means of the electric current.

Already J. STARK (loc. cit.) has carried out a few preliminary calculations on this line of thought. As at the time, however, the aerodynamic laws for greatly diluted gases had not yet been developed, his calculations are based on unsubstantiated grounds. Thus he arbitrarily assumes that after ten seconds the diffusion would make equilibrium with the mass transportation brought about by the current. Already A. WEHNELT and J. FRANK[1]) tried to find a firmer foundation for their calculation. In their experiments, just as in those by STARK, the circumstances under which the experiments were carried out, were chosen so that the carriers of the negative electricity were present only in the form of electrons. In what follows we shall extend the cases to be considered over a somewhat wider region. Let us, however, first examine on what conditions the diffusion under

[1]) Verh. d. D. phys. Ges. **12**, 444 (1910).

consideration could take place in our experiments, in which it be assumed for the present that the so highly "electrified" state of the gas has no influence on the diffusion-laws.

4. *Diffusion.*

In the mathematical treatment of this problem it should be borne in mind that in GEISSLER-tubes we have to do with a rarefied gas-atmosphere, and that the cathode and the anode space, between which differences of pressure occur, are kept separated by a capillary tube. Besides distinction should be made between the cases in which the free length of path of the gas particles *is* comparable with the dimensions of the capillary and those in which it is *not.*

For air at room temperature and a pressure of p baryes[1]) the free length of path is $\gamma = 8{,}67/p$ cm. When we have e.g. a gas pressure of 0,1 mm. Hg $= 133$ baryes, then

$$\lambda = \frac{86}{133} = 0.65 \text{ mm.}$$

I. LANGMUIR[2]) has derived that the equations holding for velocities of transfusion for gases in tubes whose diameter is not more than $2^1/_2$ times larger than the free length of path of the gas particles, are practically the same as those for which the free length of path of the molecules is large with respect to the tube-diameter.

It is now the question whether in the experiments described in the author's thesis for the doctorate the circumstances were such that always the free length of path of the molecules was greater than two fifths of the capillary diameter.

The pressure effects have been found by us down to a gas pressure of 0.087 mm. Then at room temperature:

$$\lambda = 0.65 \frac{100}{87} = 0{,}74 \text{ mm.}$$

which is about $^2/_5$ of the capillary diameter of the discharging apparatus used.

In reality, however, the gas diffusing back through the capillary, is not at room-temperature, even apart from the high "electrical" temperature[3]) of the particles subjected to the discharge. With the applied current densities the quartz capillary appeared to get heated even with air-cooling. When suddenly the current is cut out, so that the luminescence of the illuminating gas column is eliminated, it appears that with the very great current strengths previously used

[1]) Dyne/cm^2.

[2]) Gen. El. Rev. 1916 p. 1062.

[3]) Cf. J. STARK, Ann. d. Phys. (4) **14**, 506 (1904).

the outer wall of the capillary is even glowing hot. Also in view of the estimations of other observers, it cannot be considered much too high, when we put the "mean temperature" of the gas at e.g. $T_{abs} = 3000°$. Although with *constant density* the free length of path must be considered independent of the gas pressure (comp. e.g. L. BOLTZMANN [1])), it should be borne in mind on the other hand that in our experiments as a consequence of the higher temperature of the gas in the capillary, the density of the gas present there is a fraction of that which the gas would possess at the pressure indicated by the manometer at room temperature.

If e.g. for $p = 0.087$ mm. the value of λ at room temperature would already lie below the above indicated limit determined by LANGMUIR, under the circumstances of the high gas-temperature in the capillary this is not the case; i.e. for almost all the measured pressure-effects (cf. diss.) the conditions of the experiment have always been so that λ had a sufficient value in comparison with the capillary diameter to enable us to apply the diffusion formulae that refer to highly rarefied gases (on the assumption that the electric state of the gas does not influence the diffusion laws).

When M. KNUDSEN's theory [2]) is accepted, the velocity of transfusion q of a gas per second measured at a pressure of 1 barye through a tube under circumstances in which λ is large with respect to the diameter D of the tube is, according to IRVING LANGMUIR [3]), determined by:

$$q_1 = 3809 \sqrt{\frac{T}{M}} \cdot \frac{D^3}{L} (p_2 - p_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(in which M = mol. weight $p_2 - p_1$ the difference of pressure, and L the length of the capillary). When λ is small with respect to D, the formula

$$q_2 = \frac{\pi}{128} \frac{D^4 p}{\eta L} (p_2 - p_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

must be taken, in which also q_2 is based on a volume measurement at a pressure of 1 barye and η represents the coefficient of friction of the gas.

If we wanted to apply formula (2) to our observations, we should at least have to fill in the value of η for high temperatures.

For simplicity's sake, however, we fill in the value of η for air at room temperature, viz. 181.10^{-6} C. G. S. units. Further on we shall state results which enable us to make our choice between equations 1 and 2. Then formula 2) becomes:

$$q_2 = 136 \frac{D^4}{L} \cdot p (p_2 - p_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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[1]) Vorlesungen über Gastheorie 1910 p. 70—71, footnote.
[2]) Ann. d. Phys. (4) **28**, 76 and 999 (1909).
[3]) Gen. Electr. Rev. **19**, 1063 (1916).

5. *Calculation of the Pressure-Effect.*

a. It is seen that only circumstances are dealt with in which λ is "sufficiently" great with respect to D. In the thus restricted category two cases should, however, be distinguished:

I. The gas pressure is higher than 0,1 mm., and the discharge takes place at comparatively low potential differences.

II. The gas pressure is lower than 0,1 mm., and the discharge takes place at high potential differences. This category has been treated by STARK, WEHNELT and FRANK, and will be left out of consideration here. The pressure effects belonging to this are very slight, and of opposite sign to those found under I.

When the gas pressure is higher than 0,1 mm., and the potential of discharge is slight, both the positively and the negatively charged particles may be considered to be at least partially loaded with matter. Let us suppose for a moment that all the charged particles are in this case.

Let us consider the conduction of electricity through a gas, that contains only univalent ions, in a cube the sides of which are 1 cm. long, the direction of the current being parallel to one of the sides. When in this cube the direction of the electromotive force be taken as x-axis of a system of coordinates, then with a potential difference v between the end-planes, a positively charged particle undergoes an acceleration expressed by the known equation of motion:

$$m_p \frac{d_2 x}{dt^2} = eV$$

(In this e is the charge, m_p the mass of the positive ion). The electric force acts undisturbed on the charged particle during a time which elapses between two collisions. Be λ_p the mean free length of path, and c_p the mean velocity of the positive ion, this time is on an average $= \tau = \frac{\lambda_p}{c_p}$.

By integration of the equation of motion, taking the value of τ into account, summation of the components of velocity for all positively charged particles n, per volume unit, the formula

$$\frac{n_1 e V \lambda_p}{2 m_p c_p}$$

is found [1]) for the number of positive ions that passes per second through the cross-section of the conductor.

Likewise follows from the theory of the conduction of electricity through gases for the number of negative ions:

[1]) Cf. e.g. G. JÄGER. Theor. Phys. IV. Samml. G. § 57, 61.

$$\frac{n_2 e V \lambda_n}{2 m_n c_n}.$$

When on discharge every positive ion gives a_1 gas molecules, and every negative ion a_2 gas molecules, it is seen that at the cathode per unit of time the number of gas molecules plus ions will be diminished by:

$$\frac{n_2 e V \lambda_n a_2}{2 m_n c_n} - \frac{n_1 e V \lambda_p a_1}{2 m_p c_p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

whereas at the anode a corresponding increase of gas molecules will take place.

Hence it is seen that as was already stated in the author's thesis for the doctorate, the differences of pressure must depend on the number, mass, charge and mobility of the positive and the negative ions.

The supposition made here that only univalent ions would occur, does not answer to reality. Many kinds of ions will be found side by side, and at different places of the path of the current the condition differs. The current conduction is very complicated in its nature. We pointed this out already before [1]) in connection with the destructive action of the discharge on the particles affected by it. It is, therefore, to say the least of it, very hazardous to draw far reaching conclusions from the measured pressure effects with regard to the nature of the bearers of the electricity. It will always be necessary to take also other methods into account, e.g. those which have been followed with such fruitful results by J. J. THOMSON, J. STARK and others.

It is, however, possible to demonstrate, that, as regards the order of magnitude of the calculated results, the view must be valid that the mass-transportation by means of the electric current must be chiefly responsible for the observed pressure effects.

Thus considered there can be no objection to taking a single simplified case as a subject of further consideration, in which as gas nitrogen may be chosen.

b. Let us assume that per unit of time an equal number of positive, univalent nitrogen-ions leave the capillary space on one side as negative univalent nitrogen ions on the other side, and let us suppose that on discharge per negative ion one gas-molecule is supplied, whereas at the cathode two positive ions are required for this.

A gram-molecule of an ion (= 22400 ccm.) considered as gas under normal conditions cedes 96540 coulombs on neutralisation.

A milli-ampère transports per second $\frac{22400}{96540.1000}$ ccm. of gas under

[1]) L. HAMBURGER. Chem. Weekblad **15**, 932 (1918).

normal conditions $= 0.23.10^{-3}$ ccm. or at a pressure of p. mm of mercury.

$$\frac{760}{p} . 0{,}23 . 10^{-3} \text{ cm. gas.}$$

According to the supposition the current is conveyed half by negative particles, half by positive particles. Hence taking into consideration what was assumed above

$$\frac{760}{2p} . 0{,}23 . 10^{-3} \text{ ccm.}$$

is liberated on discharge per m.A. at the anode, and:

$$\frac{760}{2p} . 0{,}23 . 10^{-3} . \tfrac{1}{2} \text{ ccm. of "neutral" gas}$$

at the cathode.

Hence $\frac{760}{4p} . 0{,}23 . 0^{-3}$ ccm. *more* at the anode than at the cathode, or when the strength of the current is A. milli-ampère:

$$A \frac{760}{4p} . 2{,}3 . 10^{-4} . . . . . \quad (5)$$

A stationary state will occur when through the diffusion an equal amount is carried back from anode to cathode. Let us think the current cut out for a moment with given difference of pressure and all the ions re-combined to neutral molecules. Then the gas must flow black through the capillary. Let us apply for this purpose formula (1), which under these circumstances [1]) passes into:

$$q_1 = 38090 \frac{D^3}{L} (p_2 - p_1) . . . . . \quad (6)$$

When the stationary state prevails, we get [2]):

$$A \frac{760}{4p_{mm}} . 2{,}3 . 10^{-4} = 38090 \frac{D^3}{L} (p_2 - p_1)/p_b \quad . . . \quad (7)$$

$= 38090 . \frac{D^3}{L} . \Delta p$, when $p_2 - p_1 = \Delta p$ is put [3]).

Let the pressure of the gas be $p = \frac{(p_2 + p_1)}{2} = 0.15$ mm. $= 200$ baryes, $D = 0.2$ cm., $L = 5$cm.
$A = 400$ mA., then:

$$\frac{400 . 700}{4 . 0{,}15} . 2{,}3 . 10^{-4} = 8 \frac{38090 . 10^{-3}}{5 . 200} . \Delta p.$$

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[1]) Assumed is $T = 2800^{\circ}$. (water-cooled capillary wall).

[2]) p_{mm} represent the pressure expressed in millimeters of mercury, p_b that in bareys.

[3]) A factor $1/p_b$ has been added in the second member of this equation, because in equation 3 (resp. 6) q_1 (resp. q_2) is measured by the product of volume and pressure (expressed in baryes), whereas from equation 5 a volume results at a pressure p,

$$\Delta p = \frac{5 \,.\, 760 \,.\, 400 \,.\, 200 \,.\, 2{,}3 \,.\, 10^{-4}}{15 \,.\, 38090 \,.\, 8 \,.\, 10^{-5} \,.\, 4} = 335{,}5 \text{ baryes} = \boxed{0{,}29 \text{ mm.}}$$

This amount for Δp is considerably greater than the experimentally found value (viz. about $\boxed{0.08}$ mm.) with the substituted value of p. That the calculation gives a result that deviates from the value determined experimentally was only to be expected, seeing the arbitrary character of the suppositions. When e.g. in the beginning of § 5 sub *b* we had changed our assumptions in that sense that on discharge of the positive ions not 50 %, but only 15 % less molecules are formed, then on transition of the negative ions into the "neutral" gas state, we should have found for the calculated pressure effect a value of $\boxed{0.087}$ mm., which practically would have been in agreement with the empirically found value.

c. However even the supposition that an equal number of negative and of positive ions take part in the conveyance of the current, will not correspond with reality. As will be shown presently, we should, however, have arrived at similar results, when it had e.g. been assumed that per positive ion an equal number of gas molecules are formed on discharge as per negative ion, but that a much greater part of the current-conveyance takes place by the negative ions than by the positive ones [1]).

There is, indeed, a certain ground for the supposition that a greater part of the current conveyance takes place through the negative ions than through the positive ones.

In the paper cited by us (BOLTZMANN-Festschrift 1904) STARK already used the formula $V_n = 1{,}37 \times V_p$ for air, when the positive and the negative ions are "molecule-ions", in which formula V_n and V_p are the different specific velocities of the negative and the positive ions. Also RATNER (Phil. Mag. (6) 32, 441, 1916) uses this value for normal cases, pointing out, however, that on change of the gas pressure and of the electric force, this quantity does not remain constant. When we assume the value 1,3 for the ratio $\frac{V_n}{V_p}$, the current conveyance takes place for 56,5 % through the negative ions, and for 43,5 % through the positive ions

$$\left(\frac{100}{1{,}3+1} = 43{,}5\right).$$

Among the circumstances described in this § 5 under *c* we find

[1]) It is further plausible that the too high result is owing to the fact that also in the pressure region considered here for a great part free electrons will reach the anode. This will be further discussed presently.

that in consequence of the current transportation an increase of $A\frac{760}{p}.0{,}23.10^{-3}.0{,}565$ takes place at the anode, whereas at the anode the quantity of gas is diminished by $A\frac{760}{p}.0{,}23.10^{-3}.0.435$ through the current transportation.

Hence there remains an increase at the anode of $A\frac{760}{p}.0{,}23.10^{-3}.0.13.$

In the same way at the cathode a decrease is found of $A\frac{760}{p}.0.23.10^{-3}.0{,}13.$

The difference between anode and cathode, therefore, becomes:

$$A\frac{760}{p}.0{,}23.10^{-3}.0{,}26 = A\frac{760}{4p}.2{,}3.10^{-4}.1{,}04,$$

which is practically the same as formula 5 of p. 385.

In many cases the point of issue given here will be preferable to the supposition formulated in the beginning of § 5 under *b*.

It is, however, clear that under definite circumstances negative ions resp. electrons may act as attraction nuclei. We may refer e.g. to the condensation experiments of WILSON in a nearly related case. Then it might very well happen that through the discharge of the negatively charged particles a great number of molecules is liberated at the anode.

d. Application of equation 3 yields entirely different results. Combination of this equation with (5) gives:

$$\frac{A}{4}.\frac{760}{p_{mm}}.2{,}32.10^{-4} = 136\frac{D^4}{L}\,p_b.(p_2-p_1)/p_b \quad . \quad . \quad . \quad (8)$$

Substituting the same numerical values as above we have:

$$\frac{400}{4}.\frac{760}{0{,}15}\,2{,}32.10^{-4} = 136\frac{16.10^{-4}}{5.200}.2.10^3,\Delta p.$$

$$\Delta p = 2700 \text{ baryes} = \boxed{2{,}0 \text{ mm.}},$$

which value is so many times greater than the observation in this pressure region, that it must be looked upon as of an entirely different order of magnitude.

Besides, the experiments teach that it is contradictory to reality that the pressure effect should be in inverse ratio to the gas pressure, as would ensue from formula 8. In reality within a pressure area lying between 0,2 and 0,5 mm. the value of Δp appears experimentally to vary little, if at all, with p, which is in harmony with formula 7. Hence formula 8 should be rejected. Apart from the reasons set

forth inter alia in the next paragraph, formula 7 is therefore to be preferred.

e. It should now also be pointed out that it follows from equation 7 that Δp is proportional to the strength of the current, which as was already stated by us (cf. Thesis for the doctorate) has also been established experimentally for nitrogen.

It may, however, happen that with higher current densities there appear other bearers, as e.g. is very probable for argon. It is to be regretted that sufficient quantitative data are wanting about the dependence of the pressure effect on the current density in this gas.

In general it may be said a priori that the pressure effect cannot be a simple function of the gas pressure, because, as is known, other bearers will occur for important variations of the pressure. One and the same supposition will not always serve our purpose. With very low pressures and with high potential differences electrons, instead of charged atoms or molecules, can be discharged at the electrodes to such an important degree, that the pressure effect even reverses its sign (STARK, WEHNELT and FRANK loc. cit.). In this sense we have distinguished two categories on page 383.

As was already stated at the end of § 5 under *a* the preceding calculations have, indeed, only been given to show that the difference in properties of the positive and negative ions can actually give rise to important pressure effects, which are of an entirely different order of magnitude than those which should be considered as ensuing directly from the electric wind. It is, therefore, necessary to point out here, apart from the criticism given in the following paragraph, that in general the phenomena met with, are very complicated, especially for high gas pressures. We should, therefore, not be very optimistic with regard to a satisfactory, mathematical treatment of this subject.

6. *Criticism; Modification of the Physical View.*

Both equation 7 and equation 8 have been obtained by combination of equation 5 with equations of diffusion. We remind that in § 5 under *b* it was given by way of supposition: "Let us think the current cut out for a moment with given difference of pressure, and all the ions re-combined to neutral molecules. Then the gas must flow back through the capillary." After this the diffusion laws are applied.

In reality, however, the measurements are made, while the current has *not* been cut out.

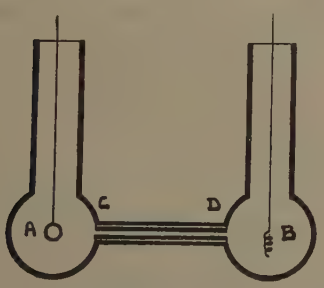
Then exceedingly important processes take place in the capillary

tube through which the gas flows. We are not justified in accepting the diffusion formulae 6 or 3 there without reservation. On the contrary. On similar grounds as before on another occasion we rejected any thermodynamic calculation of electro-chemical gas-reactions on principle, we cannot unconditionally accept the application of the normal diffusion formulae here. For brevity we refer to the part dealing with this point of the cited paper.[1])

It seems, however, not devoid of interest, to demonstrate some points also in a direct way.

We stated already that $\frac{760}{p} . 2,3 . 10^{-4}$ ccm. of univalent ions are transported per mili-ampère.

When we substitute in this e.g. $A = 435\ mA$ $p = 0,76$ mm., it would follow that also in the stationary state 96 ccm. (reduced to room-temperature) of gas flowed per second from the capillary, though the capacity of the whole capillary is only 0,2 ccm.; moreover it should be considered that the gas in the capillary possesses a very high temperature, hence a very slight density. This is untenable. Though from the fact that the pressure effect at the anode (for the given value of p) corresponds to an increase of pressure, we must conclude that at the anode a considerable quantity of charged atoms and molecules is discharged, we must certainly derive from the just given numerical example that the conduction of electricity in the luminous column takes place in a very important degree by free electrons, which are charged partially with matter (see figure) when entering the spherical space A. Further divested of any mathematical garment, the physical view arrived at must really deviate from that which led to the combination of equation (5) with the diffusion-equations.



The application of the ordinary diffusion laws referring to the reflux of gas through CD now appears to be very questionable indeed. *For the gas-molecules, which have partly originated through the discharge of ions at the anode, and are going to leave the space A for C, will for the greater part be scattered and charged by the electrons rushing from CD, after which they are again subjected to the electric field.*

When it is finally assumed that for pressures ranging between 0,4 and 1 mm. no great variations in the bearers of the electricity

[1]) L. HAMBURGER. Chem. Weekblad **16**, 664 (1919).

take place, the slight variability of Δp with the gas-pressure, which has been observed in this region for different gases, becomes explicable also in this way (cf. e.g. Diss. p. 92).

The increase of Δp with the current density is also easy to see. For in the case that the nature of the bearers is not modified with the current density — which may be assumed with a single exception (argon) for the region examined experimentally, the following formula may be substituted for formula 5:

$$q = \frac{1}{a} \cdot A \cdot \frac{760}{p} \cdot 2{,}32 \cdot 10^{-4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in which at constant gas pressure and not greatly varying tension a is a constant whose value is many times the unit. Putting:

$$\frac{760}{ap} \cdot 2{,}32 \cdot 10^{-4} = b$$

(9) becomes

$$q = b \cdot A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

We can also say something further about the diffusion: Both formula (1), and formula (2) show that the diffusion varies directly with Δp. In connection with the electrical conditions it must also be a function of variables of electric nature. The only motive force for the diffusion is, however, Δp; therefore the reflux must always be proportional to it. Hence may be written:

$$q = \Delta p \cdot \varphi(x, y \ldots) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

As soon as a few more ccm. of the greatly rarefied gas have entered the anode space, the stationary state sets in.

Combination of (11) with (10) gives:

$$b \cdot a \cdot = \Delta p \cdot \varphi(x, y \ldots)$$

or

$$\Delta p = A \; b \cdot \Phi'(x, y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

through which the proportionality of Δp with A finds expression.

7. *The Centres of Luminescense.*

a. Making use of the obtained experimental measurements regarding the intensity of light-emission of gases and mixtures of gases at electrical discharges, we have devoted some attention in our Thesis for the Doctorate to the consideration of the mechanism of electroluminescence. Also in connection with the pressure-effect studied more fully here, we will consider some points somewhat more closely.

Let us first remind of this that the objective measurements of intensity taught that the intensity of the emission of light of a gas is in direct ratio to the supplied energy, if not on change of the

electric variables a change in the character of the centres of light-emission takes place.

After J. STARK had already derived this theoretically for slight optical thickness (Ann. d. Phys. (4) **14,** 506, (1904)), C. D. CHILD has returned to this subject in some papers (Phil. Mag. (6) **27,** 278 (14); Phys. Rev. (2) **15,** 33 ('20)).

From the fact itself that the quantity of emitted light is approximately proportional to the current strength, follows that in principle the emission of light is owing neither to ionisation, nor to recombination (after previous ionisation). It is known that it has been made experimentally probable, that emission of light can take place also without ionisation. It is, indeed, in agreement with the theory of BOHR c.s., which states that radiation takes place when an electron crosses from a path that lies more on the outside to one that lies more on the inside of the atom, to which the supposition may be added that in most cases of electric discharge the electron that changes from one path to another, has never been entirely separated from the nucleus.

CHILD shows that if the emission of light were owing to the recombination of ions, this emission would have to be approximately proportional to the second power of the current strength, and the same thing would hold, when ionisation was considered as the cause of the light emission. While the number of recombinations resulting from complete ionisation depends on the product of positive and negative ions, and is, therefore, proportional to the second power of the electrons present, the number of partial ionisations [1]) depends only on the number of electrons present that gives rise to the partial ionisation. Consequently this is proportional to the first power of the electrons present.

The previous calculations [2]) have taught that free electrons are really present in the luminous column in great numbers, and that they bring about the current conveyance in a preponderating degree. This proves that the current is approximately proportional to the number of electrons present. The number of partial ionisations is proportional to the latter, from which the proportionality of the light-emission to the current strength follows directly. For it will readily be seen that the number of recombinations ensuing from partial ionisation is in direct ratio to the number of partial ionisations.

b. It is clear that a more accurate knowledge of what takes place with mixtures of gases, can give us a clearer insight with regard to

[1]) Let by partial ionisation be understood the increase of the distance of one of the electrons from the atomic nucleus, without it breaking away from it.

[2]) Cf § 5*c.* note and § 6.

the centres of the light emission on electric discharges also for simple gases. In consideration of previous researches on collisions of electrons with gas molecules FRANK and HERTZ defined a theoretical view about mixtures of gases more closely, assuming that in electro-positive and in the rare gases the electrons collide elastically with the gas molecules, so long as the energy does not exceed that amount that corresponds with the ionisation-potential. They derive that with mixtures of gases the light-emission takes place preponderantly through the gas with the slightest ionisation-potential. Indeed, in many cases this theory appears qualitatively to harmonize with experience. Already in our Thesis we drew attention to the deviation in mixtures of argon and mercury, and in the Zeitschrift für wissenschaftliche Photographie (18, 43, ('18)) we pointed out that our experimental result in the field of spectral intensity confirms the opinion that for mercury the determination of the potential of ionisation at 10 Volts is preferable to the value given earlier by others (5 Volts). We have, however, also drawn attention in our "Thesis" to objections to the theory of FRANK and HERTZ, among other things on the ground of the fact that light-emission can also take place without ionisation. Indeed, FRANK and HERTZ themselves have published a modification of the theory in question in connection with BOHR's results (Phys. Zeitschr. 20, 132 ('19)).

The necessity of this modification follows particularly from the fact that also with values lying below the ionisation-potential electric discharges through gases can take place. Accordingly FRANK and HERTZ abandoned their view of the perfectly elastic collision, and like CHILD, they assumed in agreement with BOHR's theory, that when an atom collides with an electron, and the energy of the latter is sufficient, one of the electrons of the atom can pass from its path to one lying more on the outside. It is now conceivable that a return to the normal path takes place with light-emission, but also that before this happens, the injured atom again collides with another electron, so that a further change of path takes place etc. etc., till at last the partial ionisation can have changed into a complete ionisation.

c. So it is seen here that the optical phenomena compel us to assume dislocated atoms. Even in case of a rare gas multifarious particles will occur in the path of discharge according as the dislocation of the atoms takes place to a greater or less degree. When we have to do with molecules, i.e. with atom complexes, the question will be much more complicated. For of each of the atoms in the molecule one of the electrons in the "outer path" of the atom in question can be in an abnormal condition. To this complicated

state of the innumerable kinds of dislocated molecules corresponds the enormous complexity of the molecular spectra.

This is of importance for the chemist. The fact in itself that the determination of the chemical and optical properties is attributed to the electrons of the "outer shell", shows clearly the great importance for the chemist to know the laws that govern the optical properties, because this must give him a clearer insight in the laws controlling the chemical properties. But besides H. J. PRINS [1]) pointed out already in 1912 that the same factors that influence the chemical properties, influence the catalytical properties in an analogous way. We think we are justified in concluding from this that the outer electrons also determine the catalytical properties [2]). Now it is exceedingly remarkable that it appeared necessary for the explication of the catalytical phenomena to introduce the conception of dislocated molecules, resp. atoms, (J. BÖESEKEN) [3]) long before the above results had been established in optical region. Hence we meet with a proof for the existence of dislocated states in two widely divergent regions. It seems to us that this train of reasoning is of importance for the further substantiation of the theory of catalysis, as given above.

d. In connection with what precedes it is also necessary to devote some attention to the law of displacement enunciated by W. KOSSEL and A. SOMMERFELD (Berichte der Deutsche phys. Ges. 21, 244, 1919), which states that the spark spectrum of every element has the same character as the arc-spectrum of the element which precedes it in the periodic system. As early as 1916 W. KOSSEL (Ann. d. Phys. (4) 49, 229, 1916) had found a connection between molecule-formation and atomic structure, in which among others as basis the assumption was accepted that the elements from every vertical row of the periodic system are characterized by the same definite number of outmost electrons, which number, rising to the number of 8, is every time 1 more than that of the preceding vertical row.

When through ionisation an electron is withdrawn from the atom, it shifts with regard to its optical behaviour, which as we saw is determined by the outmost electrons, to the preceding vertical row.

This view teaches us that also on complete ionisation the light-emission is chiefly determined by the rest of the atom ion that is left behind, and not by the return of the removed electron to the ion.

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[1]) Thesis Delft 1912. Journ. f. prakt. Chem. 89 (1914).

[2]) Cf. also L. HAMBURGER. Chem. Weekblad 16 (1919).
A. E. LACOMBLÉ, Zeitschr. f. phys. Chem. 93, 269 ('19).

[3]) Cf. e.g. J. BÖESEKEN, These Proceedings 1914.

e. And this forms in our opinion the connecting link to the view recently set forth by J. J. THOMSON, according to which he assumes that electro-luminescence radiation chiefly takes place with recombination of free electrons with ions (Phil. Mag. 37, 419, 1919) [1]).

It seems to me that after the above remarks some difficulties would have to be removed if this view is to be maintained. But it *is* clear that particularly when radiation is excited by a strong external electric source of energy, ions must appear, and to these rests themselves the strong emission of light is, in fact, chiefly owing.

That on combination of the ion with an electron a great disturbance in the molecule takes place, which likewise gives rise to light-emission of the different "erregte" states, is clear. That such an emission of light takes place in case of the return we have discussed, has experimentally been made very probable by P. LENARD for the region of phosphorescence.

8. *Summary.*

As a summary we may give the following conclusions from some results of the author's Thesis for the Doctorate and the preceding calculations:

1. The observed pressure effects are chiefly owing to the difference in the number of molecules that arises on the discharge of the positive and negative ions at anode and cathode. In direct sense the electric wind plays only a very subordinate part. The extent of the pressure differences varies with number, mass, charge, mobility of the positive and the negative ions. Hence the dependence on the electric variables, the gas pressure, the nature of the gas.

It appears possible to come to a physical interpretation of the factors, leading to the pressure effect (Δp), the consequences of which are also in harmony with the dependence of Δp on different. variables.

2. There occur positive and negative ions charged with mass in the luminous positive column, and also electrons in a considerable degree. The current-conveyance is chiefly brought about by the latter.

3. The conclusions under 1 and 2 form in the region of electro-luminescence experimentally and logically a support for the theories and views of CHILD, FRANK, and HERTZ, and to a certain extent to those of THOMSON as indicated above.

4. The outer electrons of the atom determine the catalytic properties. The right of existence of the assumption of dislocated states in the theory of catalysis is optically confirmed.

Dordrecht, March 1920.

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[1]) Cf. also Engineering 107, 410 (1919).

Geology. — *"On the Relation between the Pleistocene Glacial Period and the Origin of the Sunda Sea (Java- and South China-Sea), and its Influence on the Distribution of Coralreefs and on the Land- and Freshwater Fauna"*. By Prof. G. A. F. MOLENGRAAFF and Prof. MAX WEBER.

(Communicated at the meeting of November 29, 1919).

I. GEOLOGICAL PART by G. A. F. MOLENGRAAFF.

The continental shelves and the agents at work in their formation.

It is a well-known fact that continents are encircled over large distances by shallow seas deepening gradually down to about 100 fathoms. Farther seaward this depth progresses more rapidly, until the average ocean-depth is attained.

The floors of those shallow seas are together known by the comprehensive name of *"the continental shelf"*. The total area of this shelf is according to MURRAY about 25 million km.².

In most textbooks the way in which the continental shelves originate is seldom explained, and their existence is generally put forward without comment as something quite natural. Moreover in the European geological literature the problem of their origin belongs to the more or less neglected subjects. This is the more remarkable since the existence or the non-existence of shelves and the manner in which they develop is apt to throw much light upon the geological history of the region concerned.

Shelves must arise along the borders of every continent as long as its position relative to the sea-level remains constant; then the shelf is built up and enlarged by the sediments transported to the sea through the various denuding agents [1]) which act upon the land [2]). The more denudation progresses, the more it becomes obvious that the

[1]) Including the action of the surf, i.e. the abrasion at the coasts, and the formation of the plane of abrasion.

[2]) As long as the position of the land relative to the sea remains stable, the area of the shelf will grow towards the sea. Towards the land, however it will lose ground, because the peneplain not only broadens towards the land with increasing denudation, but also in some degree encroaches upon the shelf through accretion.

circum-continental shelf is the submarine prolongation of the peneplain above the sea-level [1]). The seaward growth of the shelf comes to an end only as soon as the continent concerned will have been eroded to about its base-level, i.e. has become a perfect peneplain.

Of the latter no instance can be pointed out, because the process of shelf-formation is repeatedly (though with intervals of thousands of years, we may nevertheless use this word geologically) modified by relative movements of land and sea.

To get a clear insight into the influence of these movements on shelf-formation, it will be convenient to apply the term *gradation-plane* to the plane which comprises the combined peneplain and shelf. The shelf is the submerged portion of the gradation-plane, whereas the peneplain represents its emerged portion.

Now it is obvious that the mode of development of the shelf depends on:

1. the mode of development of the entire gradation-plane;
2. the extent to which the gradation-plane has been submerged;
3. the position of the gradation-plane.

First of all the growth of the shelf keeps pace with that of the entire gradation-plane, but besides this it also increases or decreases according to a larger or smaller portion of the gradation-plane being covered by the sea. Finally the area of the shelf also depends on the position of the gradation-plane; in case orogenetic movements cause it to shift from its original position (gently sloping towards the sea) to another, say, a more inclined one, the depth of the water on the shelf will, during these movements, increase seaward and the consequence will be that the sediments, which are transported from the land towards the sea, will become incompetent to fill up the entire available space; consequently the newly formed beds will not reach the sea-level and very little sediment will be left to build up these beds and thus to extend the shelf farther seaward.

The above-mentioned three conditions lead to the following conclusions:

1st. Diastrophism will in the first instance, nearly always check the outgrowth of the shelf, because it generally steepens the slope of the existing surfaces both above and below the sea-level, consequently also that of the gradation-plane. Initially it will give rise to steep coasts with poorly developed deep-lying shelves or none at

[1]) CHAMBERLIN unites denudation of the land and the growth of the shelf into one larger process called by him *gradation*.

T. C. CHAMBERLIN Diastrophism and the formative processes. II. Journal of Geology XXI. p. 528, 1913.

all. Very often, however, diastrophism introduces a new cycle of erosion, and consequently revives the process of denudation, resulting in the long run in intensified gradation and in growth of the continental shelf.

A lapse of time succeeding a period of strong diastrophism will, for regions affected by this process, be characterized by potent denudation, active sedimentation and a corresponding strong development of the gradation-plane, consequently also of the continental shelf.

2nd. Negative movement of the coastline, i.e. uplift of the land or lowering of the sea-level will, as a direct consequence, narrow the continental shelf, or cause it to disappear altogether, expanding the emerged portion of the gradation-plane at the cost of the submarine portion. But, on the other hand, such a movement will invigorate the erosion by lowering the baselevel and will, therefore, in the long run promote the growth of the continental shelf indirectly.

3rd. Positive movement of the coastline, i. e. subsidence of the land or rise of the sea-level, will eo ipso broaden the continental shelf by expansion of the submerged portion of the gradation-plane at the cost of the emerged portion, although in the long run its growth will be slackened on account of the baselevel being raised. Even in case, at the commencement of such a positive movement, the terrestrial portion of the gradation-plane is little developed, or wanting, circumstances are imaginable in which the shelf will grow to a large extent. This will occur during a very slow but prolonged rise of the sea-level. In this case the sea, even if the land should offer a strong resistance, will be able to conquer a vast territory, to destroy the land down to the plane of abrasion, and to incorporate the latter with the shelf. A small island may be altogether truncated and converted into a very shallow submarine bank, probably gently inclining towards the side where the influx of the sea came from i. e. from where the prevailing winds were blowing.

It stands to reason that, during a positive movement, the above extension of the continental shelf will be more rapid and far-reaching in case this movement has been preceded by a period of stability of the land, in other words by a period of peneplanation. For in that case the sea needs not gradually destroy and clear away the land in order to form a plane of abrasion and to incorporate it into the shelf; on the contrary, it finds a peneplain ready made, i. e. a vast area of low land easy to invade and to convert into a shelf.

This will hold all the more when the period of stability is preceded by one of diastrophism, since in that case the processes of penetration and sedimentation being invigorated, the shelf and the adjacent peneplain will be strongly developed [1]) the moment that the transgression of the sea sets in, resulting in optimal conditions for the extension of the continental shelf.

Whereas at present in regions, far removed from each other conspicuously large shelves occur, the question arises whether perhaps such optimal conditions for the expansion of continental shelves have existed in recent geological time.

This question will be answered here in the affirmative.

First of all the conditions for shelf-building are favourable now, because the Pleistocene and the Holocene are periods in which the processes of denudation and sedimentation (consequently also those of gradation and shelf-growth) are very active [2]), owing to the orogenetic movements in tertiary time, which are not yet abated in our time. Besides this there is one more condition that has been favourable to the extremely wide expansion of the present-day shelves. It is that after the close of the pleistocene glacial period a large part of the earth's surface has been invaded by the sea. This transgression commenced, as appears from the above, at a moment that the shelves and the adjoining peneplains had already been strongly developed in consequence of the late-tertiary orogenetic movements. The object of this paper is to demonstrate, for one of the largest shelves of the earth, that it owes its origin to the optimal conditions for shelf-formation, which appeared after the close of and in consequence of the pleistocene glacial period.

Influence of the pleistocene glacial period on the position of the sea-level.

What has been the influence of the glacial period on the general position of the sea-level?

In the Pleistocene age (the so-called ice-age) the ice-caps of considerable thickness and extent, which then covered a vast portion of the land

[1]) Isostatic upheavals of continents will, at least initially, also counteract the seaward accretion of shelves. The plastic movement of the continents towards the sea (*continental creep*, vide T. C. CHAMBERLIN l.c. p. 585, 1913), on the other hand, promotes the development of the shelves. These two factors will be neglected in this paper, because their influence can only be negligibly small as compared with other influences in the region to be discussed here, viz. the East-Indian Archipelago.

[2]) BARRELL in his interesting study on "Rhythms in denudation" considers the present time as one in the history of our Earth, in which the rate of the continental denudation process is very high. J. BARRELL "Rhythms and the Measurements of Geological Time". Bull. of the Geol. Soc. of America XXVIII, p. 775, 1917.

in high latitudes in and about the polar regions, and to a smaller degree also the large snowfields and glaciers in the mountains outside these polar regions, must have abstracted large quantities of water from the oceans. Owing to this the water in the oceans must in the early pleistocene period have sunk relatively to the land.

After the close of the ice-age i.e. at the end of the pleistocene period, the ice-caps in the higher latitudes dwindled down to their present state.

The melting of these ice-caps caused the water to return to the oceans, so that the latter have now almost regained the level they had before the beginning of the pleistocene period. This implies that, from the end of the pleistocene period up to the present day the sea-level along all the coasts of tropical regions must have risen relatively to the land. Everywhere in the tropical regions the sea must, therefore, have encroached upon the land, and where this land rose only slightly above the sea-level, the horizontal extent of territory invaded by the sea since the close of the pleistocene period must have been considerable. PENCK [1]) has given us a clear exposition of the influence of the pleistocene ice-age (in other ice-ages the same must have taken place) on the sea-level as early as 1882. Opinions may differ about the degree of oscillation of the sealevel. Observant of some of the accessory circumstances which render the problem more intricate, calculations have been made by CROLL [2]) in 1875, by PENCK in 1882 and by DALY in 1910 and 1915. PENCK in that year arrived at the conclusion that in the pleistocene period the sea-level in tropical regions must have been 100 m. [3]) lower than at present. Afterwards, in 1894 [4]) accepting an average thickness of the ice-caps of 1000 m., he arrived at the figure of 150 m., which figure had been mentioned also by VON DRYGALSKI in 1887. DALY [5]), who also assumed that the maximal

[1]) A. PENCK "Schwankungen des Meerespiegels". Jahrb. der geogr. Ges. zu München VII, 1882, p. 47. In the main PENCK's statement seems to me undeniable. It may be called a theory rather than an hypothesis.

[2]) J. CROLL. Climate and time, Londen 1875.

[3]) PENCK arrived at this figure (l.c. p. 67) on the supposition that in the pleistocene age the phenomenon of glaciation was not restricted to one hemisphere only, but affected both hemispheres simultaneously, a statement which we endorse here. — In case in the pleistocene age the powerful glaciation had been restricted to the northern hemisphere only, the position of the general sea-level would, according to PENCK, (l.c. p. 29) then have been at least 50, and at most 66½ m. lower than at present.

[4]) A. PENCK. Morphologie der Erdoberfläche II. p. 660, 1894.

[5]) R. A. DALY. Pleistocene glaciations and the coral reef problem. Amer. Journal of Science XXX, p. 300, 1910 and The glacial-control theory of coral reefs. Proc. of the Amer. Acad. of Arts and Sciences LI, p. 173, 1915.

development of the ice-caps in the pleistocene age was attained simultaneously all over the earth, and that their average thickness amounted to 1100 m., estimated that, since the close of the pleistocene ice-age the sea-level has been raised by an amount ranging between 23 and 129 m., most probably between 50 and 60 m.

Certain accessory factors render the problem more intricate, as has been stated above. There are in fact still other phenomena that may give rise to changes in the relative position between land and sea and thus engender movements which either run parallel, or in an opposite direction to the above-mentioned.

Among these phenomena the following have something to do with the glacial period:

1. fluctuations of the sea-level, caused by the fact that, the more the ice-caps grow, the more their attractive power upon the water of the oceans will increase, while the same will decrease again on the melting of the ice. This modifies the position of the sea-level all over the earth, but this modification is of some consequence only in the immediate neighbourhood of the ice-caps and there manifests itself by a rise of the sea-level. The corresponding sinking of the sea-level everywhere else on the earth, which will be most manifest in the regions farthest removed from the glaciated areas, is not considerable; the assumption is admissible that, during the maximal glaciation in the pleistocene age in the tropical seas, i. e. in the East-Indian Archipelago, it amounted to 10 m. or about 5 fathoms at most [1]).

2. Fluctuations of the sea-level caused by the water being driven back into the oceans by the ice. In the polar regions the water of the sea is driven back from the coast over some distance by the

[1]) This figure we borrow from DALY's "Glacial Control Theory of Coral Reefs" p. 174. DALY has derived it from calculations given in R. S. WOODWARD's "On the Form and Position of the Sealevel". Bull. 48 of the U.S. Geol. Survey 1888. Here, however, we do not find discussed (see note p, 78) the results obtained by E. VON DRYGALSKI in "Die Geoidformation der Eiszeit". (Zeitsch. der Ges. für Erdk. XXII p. 169, 1887). In this paper VON DRYGALSKY brings back to due dimensions the attractive influence on the sea-level of the ice-caps, accumulated in the ice-age on continental landmasses, which influence had been overrated by PENCK. It deserves attention that all these calculations have been made more or less based on the theory of CROLL, who held that during the glacial period only one of the hemispheres had been intensely glaciated, the other hardly or not at all (J. CROLL "Climate and Time" especially Chapt. 23 London 1875). It will be useful to make new calculations of the influence of the attraction of land-ice on the general form of the sea-level, based on the now generally accepted hypothesis that during the ice-age the glaciers and ice-caps have been all over the earth larger then now.

land ice, which is moving seaward. This repulse was more intense in the ice-age than now. Von Drygalski believes that in the ice-age the general sea-level must in consequence of this phenomenon alone have been raised 6 m. [1]).

3. Fluctuations of the sea-level, caused by elastic downward movements of the earth's crust under the weight of the accreting land-ice, succeeded on melting, with some retardation, by contrary movements of about equal amount. These important movements are restricted to the regions that were covered by the land-ice, as has been proved principally by repeated careful researches in North-America [2]); they cannot have exerted a powerful influence upon the height of the sea-level, except in the glaciated regions and their immediate vicinity. In tropical regions these movements will only have resulted in a slight lowering of the sea-level, during the period of growth, and by a corresponding rise of the sea-level during and after the retreat.

In tropical regions, therefore, as appears from the foregoing, all these additional influences are so little effective that the main phenomenon cannot be largely modified by it.

Careful consideration of all the calculations that came to my knowledge, justifies, I think, the assumption that the collective result of all the above-named influences, which, as already observed, partly co-operate, and partly counteract each other, has been that during the periods of maximal expansion of the ice-caps in pleistocene time, the sea-level in tropical regions (viz. the regions farthest removed from the large centra of ice-accumulation) must have been at least 40 fathoms (72 m.) lower than at the present day. Daly [3]) estimated this figure at 33—38 fathoms, or 60—70 m.

The relations between land and sea, however, are also influenced by crustal movements which are quite independent of the glaciation. I refer first of all to orogenetic movements of the land, generating apparent movements of the sea-level, manifesting themselves in shifts of the coast-line, which are not infrequently considerable. They occur all over the earth, but exclusively in tectonically active regions.

Finally the relations between land and sea are still modified continually everywhere by shifting of the shore-line, consequent on the growth of alluvial deposits, derived from the land by the destructive and transporting action of water and wind, secondly by the continuous process of filling-up of the ocean-basins by sediments and

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[1]) E. von Drygalski l.c. p. 199.

[2]) Vide: H. E. Fairchild. Postglacial uplift of Northern America. Bull. of the Geol. Soc. of Amer. XXIX, p. 187, 1918.

[3]) R A. Daly l.c. p. 174, 1915.

thirdly by isostatic uplift of the land, which latter considerably retards the effect of denudation. For the present I will leave those phenomena out of consideration, because they cannot materially have affected the oscillations of the sea-level dealt with in this paper.

The validity of the above theory can hardly be called in question, anyhow not if we assume that in the glacial period ice-masses of considerable thickness, on an average 1000—1200 m., were accumulated over a vast extent on the land in polar regions. Thus far, however, its validity has not been tested for considerable areas of the earth's surface by the relations observable at present along the coasts.

In tropical regions these tests will be simpler and must yield more precise results than outside the tropics. For outside the tropics, especially in the regions bordering immediately on the regions glaciated in the ice-age, the phenomenon of shifts of the sealevel, depending on the greater or smaller extent of the polar ice-caps, is rendered indistinct through the interference of the above-named influences, which are very operative outside the tropics, and on the contrary are hardly perceptible in the tropical regions [1]).

Furthermore, such a test can be effectual only in regions not affected by tectonic movements since the close of the Pliocene.

There is, therefore, a reasonable chance of the possibility to trace and to discriminate the displacements of the shorelines, caused by the

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[1]) This does not mean to say that the oscillations of the sealevel in consequence of the pleistocene ice-age are not distinguishable in temperate zones. It will be more difficult to identify the phenomenon there, since it has first to be severed from the additional influences mentioned above, whose magnitude relative to that of the main phenomenon, is not sufficiently known. On the other hand, there is a factor that could be utilized in the neighbourhood of the glaciated regions, viz. the fact that there the consecutive glacial and interglacial periods will manifest themselves through variations in the marine fauna. At the commencement of the glacial period the first approach of the ice in the northern hemisphere will have revealed itself by the introduction of arctic types into the marine fauna. We know that this is noticeable in the latter part of the pliocene period in England and in Holland, and that, therefore, the assertion that the ice-age commenced already in what is generally called "Upper Pliocene", is not unfounded. In tropical regions, on the contrary, the alternate interglacial and glacial times will presumably not have exerted an appreciable influence upon the fauna, so that in this respect the researches in tropical climes will have to do without a factor that is available outside the tropics. Taking everything into consideration the shift of the coast-line consequent on the alternate growth and melting of the polar ice-caps, will prove to be so much more regular and less modified through other influences in the tropical regions than elsewhere that a critical examination in the tropical regions is far preferable to one in the temperate zones, at all events a far as the main features of the phenomenon are concerned.

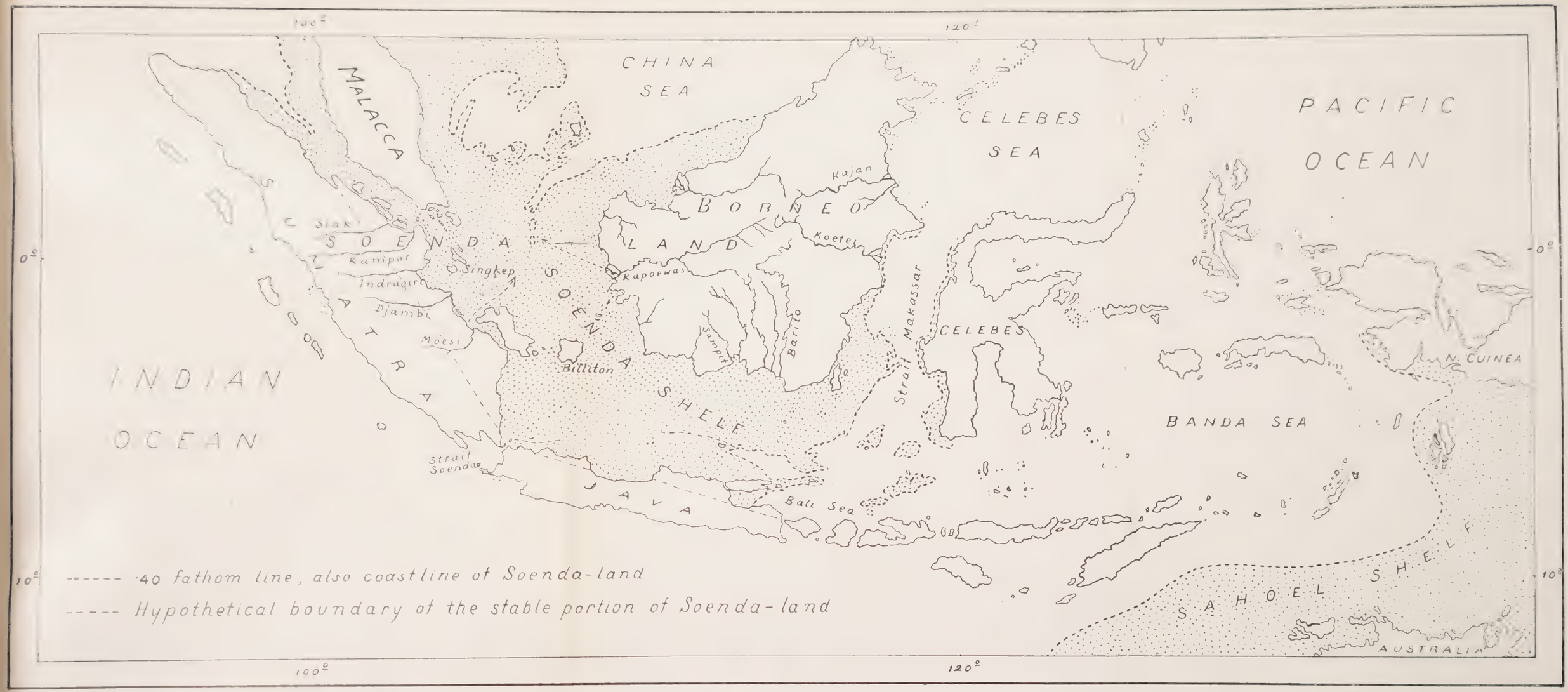

Fig. 1. Sketch-map of the East-Indian Archipelago showing the Sunda-shelf and the Sahul-shelf.

Scale 1 : 12.500.000.

variations of the extent of the glaciated areas in and after the pleistocene period, with certainty in tropical regions, especially in those that have maintained their stability ever since the commencement of the Pleistocene.

In the following pages we purpose to consider the relations between land and sea, the submarine topography and the distribution of the coral-reefs in a portion of the East-Indian Archipelago, in connection with the pleistocene ice-age.

The stable and the unstable part of the East-Indian Archipelago.

In the East-Indian Archipelago we distinguish two strongly contrasting portions, one with an exceptionally uniform and undisturbed submarine topography and another with a strikingly complicated submarine relief. Both areas are indicated on the accompanying sketchmap (Fig. 1). To the former belong the Sunda Sea and the Sahul Bank, to the latter all the other seas of the East-Indian Archipelago.

It deserves notice that this contrast has already been observed by W. EARLE as early as 1845 [1]). He termed the Sunda shelf the *Great Asiatic Bank* and the Sahulbank the *Great Australian Bank*. He noticed the unvarying mean depth of the sea above those banks, estimated by him at 30 fathoms and called attention to the fact that the character of the land and the coasts surrounding these banks is very similar and differs largely from that of the other regions in the Indian Archipelago.

[1]) W. EARLE. On the Physical Structure and Arrangement of the islands of the Indian Archipelago. Journ. Royal Geogr. Soc. XV. p. 358, 1845.

EARLE says l. c. pag. 359:

These banks, which extend from the continents of Asia and Australia, form very remarkable features in the geography of this part of the world, and, as such, are deserving of more attention than has hitherto been bestowed upon them, since it will be found that all the countries lying upon these banks partake of the character of the continents to which they are attached; while those which are situated on the deep sea which separates them, are all of comparatively recent volcanic formation, with the exception of a few small coral islands, which, in all probability, are constructed upon the summits of submerged volcanoes. The depth of water on these banks averages about 30 fathoms, deepening rapidly as the edge is approached, and shoaling gradually towards the land. It will be seen that the one I have termed the Great Asiatic Bank extends into the Archipelago from the south-eastern extreme of Asia to a distance of nearly 1000 miles, in fact to within 50 miles of Celebes, and I strongly suspect that it will be found to extend to the south-western extremity of that island also; but as there is a space of nearly 30 miles across which no soundings have been carried, I have preferred reducing the bank to the limits for which we have actual data.

VERBEEK, in his report on the Moluccas [1]), was the first to contrast these two tracts geologically. On the basis of somewhat different geological conceptions the present author [2]) did the same in 1912.

Thus the latest geological history of the East-Indian Archipelago teaches us that the two first-named shallow seas or shelves form parts of larger tracts, which have recently, anyhow after the Pliocene, maintained their stability and, putting it geologically, have behaved "continentally", whereas all the others belong to unstable portions or geosynclines, which were orogenetically active in the same time.

It thus appears that in the East-Indian Archipelago adjoining portions of the earth's crust have behaved very differently in recent times; in the stable portions the consequences of the oscillations of the sea-level in connection with the ice-age will be easily distinguishable and unmodified; in the unstable or active portions these oscillations must have occurred just as well, but their traces will be distinguishable only where they have not been effaced or modified too much by the influence of diastrophism, or in other words by the orogenetic movements of the land. This is a very favourable circumstance, as it enables us to test the theory concerned, in different ways.

How the Sunda Sea originated.

In the year 1916 the author briefly pointed out the probability of a causal relation between the origin of the above-named remarkable shallow seas of quiet submarine topography and constant depth, and the pleistocene ice-periods [3]), and has put forward his view that both the Sunda Sea, and the Sahul Bank originated from the submersion of a low land by the rise of the sea-level in consequence of the melting of the great ice-caps of the pleistocene ice-age.

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[1]) R. D. M. VERBEEK. Molukken verslag. Geol. verkenningstochten in het oostelijke gedeelte van den Ned. O.-I. Archipel. Jaarb. v.h. Mijnwezen XXXVII. p. 797, 1908.

[2]) G. A. F. MOLENGRAAFF. On recent crustal movements in the island of Timor and their bearing on the geological history of the East-Indian Archipelago. These Proceedings Vol. XV, 1, p. 232, 1912.

[3]) G. A. F. MOLENGRAAFF. The coral-reef problem and isostasy. These Proceedings Vol. XIX. p. 612, 1916.

N. WING EASTON followed a similar line of reasoning when discussing the origin of the tin-deposits in the Dutch East-Indies. Vide: "Het ontstaan der tinertsbeddingen in Indië, Weekblad de Ingenieur, 12 Maart 1919.

The name of Sunda Sea is proposed here for the shallow sea between Malacca, Sumatra and Java on the one side and Borneo on the other side, which embraces the whole of the Java Sea and the southernmost portion of the China Sea. At present no one collective name used for these various seas, but geographically as well as genetically they form one indivisible whole. NIERMEYER [1]) applied the name of Sunda Shelf [2]) to the floor of the shallow sea between Sumatra, Java and Borneo, already in 1911. I agree with him, but I apply the name to the entire shelf which has derived its origin from the submersion of the majority of the peneplanized portions of the Sunda Land (to be defined later on).

The way in which the low land originated may be conceived as follows:

Before the beginning of the pleistocene period, i.e. towards the termination of the Pliocene, what we now call the Sunda Sea was presumably taken up by rather low land, or by a group of islands. We may imagine a partly developed peneplain, covered here and there by a shallow sea [3]).

At the commencement of the pleistocene period the sea retreated in consequence of the growth of the ice-caps and thus one continuous tract of land was formed, the Sunda Land, uniting the present islands of Sumatra, Borneo and Java. It was not a high land, but on an average it stood at least 70 m. above the sealevel.

In the pleistocene age followed a period of prolonged erosion, which had become particularly active by the lowering of the base-level. Owing to this the pre-existing imperfect peneplain was greatly enlarged and perfected. Only these areas, which offered great resistance against erosion protruded as hills, so-called monadnocks, from the great plain. This large peneplain was bounded on the south, the southwest and the west by the partly volcanic, partly non-volcanic mountain-ranges of Java and Sumatra, on the north and north-east by the granitic nucleus, the high sandstone-tableland, and the mountain-ranges of Borneo. In this broad peneplain probably all the water that flowed down from those two mountainous regions in opposite directions, collected into a few large streams. One of those streams must have flowed through the region where the present

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[1]) J. F. NIERMEYER. Barrière-riffen en atollen in den Oost-Indischen archipel. Tijdschr. Kon. Ned. Aardr. Gen. 2. XXVIII p. 880, 1911.

[2]) KRÜMMEL calls this bank the Borneo-Java shelf. Its extent is estimated by him at 1.850 000 km², the depth of the sea at 50—100 m. Vide O. KRÜMMEL, Hndb. der Ozeanographie I p. 113, 1907.

[3]) This supposition is not in contradiction with the known geological data.

Java Sea extends, and, while draining the peneplain towards east-southeast, must have emptied into the most southern part of Strait Macasser. It is probable, that the vast peneplain was drained towards the north and north-north-east by another stream in the direction of the China Sea.

The hydrographic basin of those two streams must have been very large, viz. about 1.285.000 km². So, when taking an annual rainfall as great as occurs at present [1]), viz. 2,7 metres, they must have carried about 1156 cubic kilometres of water to the sea annually, i.e. about double the amount discharged by the Mississippi (552 km³) in whose basin, which is much larger (3.225.400 km²), the rainfall is much less considerable, averaging somewhat more than 52 c.m.

Presumably these streams, in spite of their little varying level, will, on account of their large mass of water, have cut their beds deep into the peneplain. Considering what takes place in other rivers in this respect, it will be safe to assume that the beds of those rivers in their lower course, must have been at least 10—15 m. deep.

After the close of the glacial period the sea-level gradually began to rise again as the ice-masses in the higher latitudes began to melt down. Then all circumstances combined to bring about optimal conditions for shelf-formation in Sunda Land. Diastrophism in tertiary time had inaugurated a period of active erosion and consequently of rapid development of the plane of gradation; the retreat of the sea at the beginning of the ice-period had operated in the same way through lowering of the base-level; inhibiting influences on shelf-formation had not occurred in Sunda Land, which had remained stable ever since the tertiary period; all this had co-operated to give rise to a plane of gradation, chiefly as a peneplain, of extraordinary dimensions. Vast tracts of land were now easily invaded by the rising sea and converted into a shelf. The Sunda-peneplain was overflowed, until the present average depth of 50 m. was reached. Thus originated the present Sunda Sea and the Sunda shelf, the largest and one of the most remarkable shelves of the world.

The larger streams were drowned and dismembered, all their tributaries becoming independent rivers, now flowing into the Sunda Sea. Several of the monadnocks were surrounded by the sea and converted into islands, as Bangka, Billiton, Singkep, the Karimata-islands, the Karimun-djawa islands, Bawean, the Arends-islands, Great- and Little-Salembouw, and numerous other small islands.

This is of course a much simplified conception of what has hap-

[1]) The volume of water discharged into the sea is taken to be $^1/_3$ of the total rainfall in the riverbasin, which rough estimate is permissible in this instance.

pened in reality. The ice-age has not been one single cold period, but a succession of colder glacial periods alternating with milder interglacial periods. Consequently the ice-caps more than once have grown to a large extent and have melted again. Thus we may surmise that during the first glacial period the Sunda-peneplain, which probably already pre-existed in an imperfect state, has recommenced to develop, that it has been covered by the sea during the first interglacial period, that during the second glacial time it was rendered more perfect, that it was flooded again during the second interglacial time and so on, until the last glacial period saw the peneplain in such a state of perfection as is now illustrated by the floor of the Sunda shelf-sea.

Many pecularities of the Sunda Sea and its surrounding coasts are in keeping with this conception or are sufficiently explained by it.

However, before dwelling on these peculiarities the following two questions must be answered:

1. how far did the pleistocene Sunda Land extend? and 2. what were its boundaries?

The Pleistocene Sunda Land.

There is one answer for these two questions: the Sunda Land is that portion of the western half of the East-Indian Archipelago which emerged from the sea during the maxima of glaciation in the pleistocene age. We take this Sunda Land to have been covered gradually by the sea to a depth of 72 m. from the last maximum up to the present day.

The Sunda Land consisted of Java and Madura, Sumatra, Borneo, Malacca, and the present sea with its islands round these countries to a depth of 40 fathoms (72 m.) as is represented on the map (Fig. 1). All that has been said, however, applies only to that part of the Sunda Land which has been stable or orogenetically inactive since the Pleistocene. The present isobath of 40 fathoms during the last maximum of glaciation in the pleistocene age, gives the ancient coast-line for that part. In order to ascertain the extent of the stable continental part of the Sunda Land it is, therefore, required to know as well the boundary between the land that has been orogenetically inactive since the close of the Pliocene, and the land that has been active. On the sketch-map this boundary has been indicated tentatively by an interrupted line. What lies within this line is the stable part of Sunda Land, to be called Sunda-land proper.

To this stable Sunda Land belongs in the first place the entire

Sunda Shelf, then also Borneo, probably with the exception of the northern part, Malacca and the eastern coastal region of Sumatra, and perhaps here and there a strip of the northern coast of Java and Madura. All the land bordering on the Indian Ocean, which belongs to the Malay geosyncline, does not belong to this Sunda Land in the strict sense of the term. Evidently this region of tectonic activity is the prolongation of the folds of the western portion of the Birma-arc, still one of the regions of the earth where the orogenetic activity is very great. It is not possible to fix the precise boundary between the stable and the unstable portion of the former Sunda Land; very likely there is no firm line of demarcation, I am inclined to class the volcanic regions, which are characterized by rocks of the Atlantic type, such as the Muriah, the Lurus and the Ringgit, under the stable region, because the Bawean-Islands with their Atlantic rocks certainly belong to it and because the volcanoes of the Malay geosyncline, like those of nearly all other geosynclines on the earth, have yielded exclusively rocks of the Pacific type. Doing so, however, the boundary-line between the stable and the unstable region must inevitably be drawn in such a way that the two regions encroach upon each other in Eastern Java. Perhaps the two relations are represented accurately in this way. The Sibbalds Bank, the Kalukalukuang Bank, the Laars Banks, the Bril, the Paternoster Islands and the Postiljon-Islands, now all coral-islands, and perhaps also the Spermonde Shelf and part of South Celebes formed, as I believe, in pleistocene time islands that belonged to the stable Sunda Land.

Now, what peculiarities are known of the present Sunda Sea, its islands and its shores?

The Present Sunda Sea.

a. General topography of the floor of the Sunda Sea and of the adjacent shores.

The Sunda Sea has a strikingly uniform depth, averaging 40—45 m., seldom exceeding 50 m. The shallowest part is that where the islands of Bangka and Billiton are situated. A depth of more than 20 fathoms is the exception there.

Excepting some gullies, larger depths than 28 fathoms (50 m.) are found only in the farthest eastern part, where the depth gradually increases towards the much deeper Macassar Strait, and also in the northern part towards the deeper basin of the China Sea and finally in the neighbourhood of Sunda Strait. The most striking characteristic of the Sunda Shelf-sea, therefore, is its *equal depth*,

the almost perfect evenness of its bottom. This is the very submarine relief that would have originated, if this sea had been formed by the submersion of a large peneplain. The particularities of this relief may be explained assuming that this peneplain discharged its water towards the Bali Sea and the China Sea, and that a bay, from the present Sunda Strait encroached for some distance on it.

For some hundreds of kilometers landward the surface of Borneo is only slightly undulating and the same is the case in the coastal region of Eastern Sumatra and on the islands in the Sunda Sea, as Bangka, Billiton, Singkep etc. The greater part of all this land partakes of the character of a peneplain [1]), rising only little above the sea-level, here and there with some gently sloping hills, consisting of rocks, which possess a more powerful resistance against erosion, emerging from the lower territory. This description applies less to the coastal fringe of Java, on which island volcanic activity repeatedly modified its sculpture and raised its level.

The slightly undulating floor of the Sunda Sea is continued, as it were, on the surrounding land. Along the coast of West-Borneo a retreat of the sea to a depth of no more than 10 fathoms would join numerous islands to the coast and enlarge the still existing peneplain of West-Borneo with its peculiar, gently sloping monadnocks, without affording any feature in the landscape to enable us to tell the old land from the new.

All the islands in the Sunda Sea, as e.g. Billiton and Singkep, present so clearly the type of regions which on account of the existence of cores of hard resisting rocks were less subject to erosion than their surroundings, that spontaneously the idea forces itself upon us to join West-Borneo to Bangka, Billiton, etc., and to consider the whole tract of the Sunda Sea as a submerged peneplain, from which the present islands rose up as monadnocks, when in the pleistocene age the sea-level was lower.

b. Character of the bottom of the Sunda Sea.

The floor of the Sunda Sea about which little is known, appears to be very muddy; the large majority of the soundings, performed in this sea, show that the bottom consists of silt or mud, whereas shells or coral-fragments are rarely reported. This can hardly be accounted for in a shallow sea like the Sunda Sea, by the influence of the rivers flowing into it now. Indeed, they transport a large amount of silt to that sea to a large distance from the coast, but

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[1]) Strictly speaking all that territory makes up that portion of the large pleistocene peneplain which has not yet been overflowed by the sea.

most likely nowhere beyond 60 km. from it. In February 1894 I found at flood-tide before the estuary of the Kapuwas in West Borneo the extreme limit of the muddy river-water as far as 50 km. from the shore [1]). When considering that the muddy fresh water, wedging out seaward very slowly, floats on the specifically heavier seawater, and that in seawater the sedimentation proceeds about ten times quicker than in fresh water, we may be sure that silt does not settle down much farther than those 50—60 km. from the coast.

When we also bear in mind that, among the rivers, debouching into the Sunda Sea, the Kapuwas and the Barito are the largest and richest in silt, we feel justified in saying that the limit of silt-deposit in the Sunda Sea lies at present between the coast-line and a distance about 60 k.m. from the coast.

The charts of this sea show [2]) however, that the bottom all over the Sunda Sea consists of silt, i.e. as far as 100 km. or more from the nearest coast.

When considering the Sunda Sea to be a peneplain, it is easy to understand that the sea, when it gradually flooded that plain received then much silt from the many rivers discharging their waters into the growing sea, this silt being deposited there at great though gradually diminishing distances from the present coast.

The silt or mud, which nearly all the soundings in the Sunda Sea have proved to be the principal constituent of the bottom, may be looked upon as a sediment carried down chiefly by the former big streams before and during the long period of gradual submergence of the pleistocene peneplain.

c. No traces of upheaval.

The shores of the islands surrounding the Sunda Sea or emerging from it, show no traces of upheaval worth mentioning. If we consider that in regions where reef-building corals live (as is the case with the Sunda Sea, though, when compared with the sea-basins of the Moluccas it is poor in reef-builders) every upheaval of the land (or subsidence of the sea-level) is almost invariably manifested by the emersion and preservation — for a long time at least — of reefs, i. e. by so-called elevated coral-reefs, it is obvious that the absence of those features nearly everywhere along the coasts of the Sunda Sea, warrants the conclusion that in the most recent geolo-

[1]) This limit is at the utmost 62 kilometers from the shore.

[2]) Since this paper was read new investigations have been made on the nature of the deposits on the floor of the Java Sea They have proved that only in the southern half these deposits consist of mud, in the northern half on the contrary they consist of sand and sandy loam.

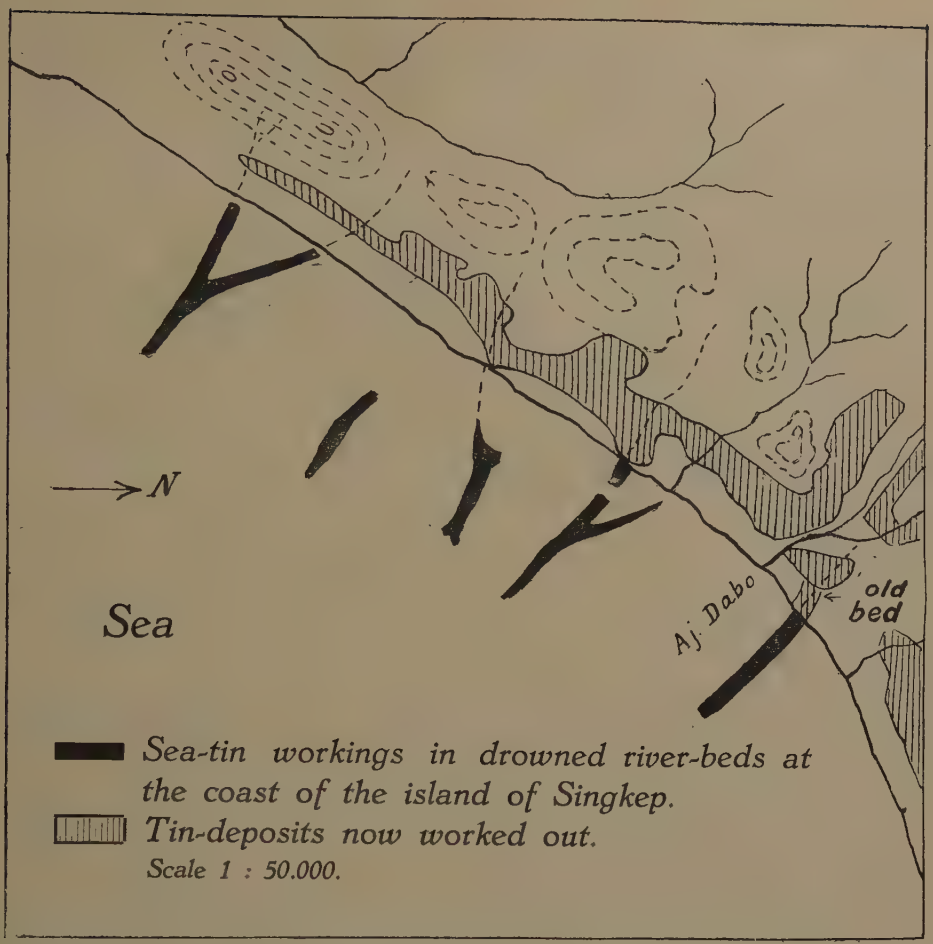

Fig. 2. After a sketchmap in possession of the Direction of the Singkep Tin Company.

gical time no negative shifts of the shore-line of any consequence have occurred there.

d. Traces of subsidence; drowned and sunken rivers.

On the contrary there are indications of subsidence of these coasts, or, which comes to the same in our argument, of rise of the sea-level.

The way in which the large muddy rivers of Sumatra and of Borneo debouch into the sea, is peculiar. The absence of deltas, as well as their wide funnel-shaped mouths — very conspicuous with the Sampit — and the great depths in the lower courses of the rivers point to positive shifts of the coast-line.

Only one of them, the Kapuwas, which carries more sediment than any of the others, has formed a delta, which, however, hardly protrudes from the coast-line into the sea.

Furthermore, the traces of the rivers of the Sunda-peneplain,

which have been dismembered and drowned through the rise of the sea-level, are clearly noticeable in the floor of the Sunda shelf-sea. The exploitation of tin-ore on the island of Singkep has revealed the existence of such drowned rivers (see Fig. 2). It has become evident that the tin-ore deposited by the running water in the deepest parts of the alluvium of the Dabo and other rivers, is still found at a considerable distance from the shore, and that the channels of the Dabo and of other rivers are traceable up to about 1500 m. from the coast. In one of those rivers, the Djangkang, the lowermost tin-bearing part of the fluviatile alluvium worked at present lies at about 17 m. below the sea-level. The stream-deposits at a distance of 1300 m. from the shore are about 10 m. thick, while the sea above them has a depth of 7 m. The exploitation of this so-called sea-tin near the island of Singkep has distinctly shown the existence of the submarine prolongation of a number of river-valleys.

This phenomenon can be readily accounted for when accepting subsidence of land or rise of the sea-level. I consider the presumption admissible, that also in the neighbourhood of other tin-islands in the Sunda Sea, as e.g. near Banca and Billiton, the existence of similar tin-deposits below the sea-level in the channels of drowned rivers could be proved. Just as near the island of Singkep, the exploitation of the sea-tin might probably prove to be of great economical importance there as well.

The gullies of the sunken rivers need not always be found extended into the sea, they may still be situated in the land, but then at such a low level, that with the present base-level of denudation (the sea-level)they could not possibly have been eroded so far by the water. The exploitation of the stream-tin, in Banca as well as in Billiton, has revealed the existence of such abnormally deep valleys. VERBEEK [1]) records several instances, of which I will mention the following:

In Banca, the pleistocene bed of the Krasak-river in the district of Pangkalpinang, which is eroded at least 16 m. below the bed of the present course; the ancient bed of the Pandji-river in the district of Blinju, lying 9.25 m. below the present bed and not much less below the sea-level; the ancient bed of the Liat-river in the district of Sungeiliat, the lower course of which lies 13—19 m. below its present bed and about as much below the sea-level;

in Billiton the ancient bed of the Sidjuk-river, which near mine

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[1]) R. D. M. VERBEEK, Geol. Beschr. van Bangka en Billiton. Jaarb. van het Mijnw. XXVI, p. 143—156, 1897.

No. 30 is 6—11 m. deeper than the present bed; an affluent of the Munsang in the district of Manggar, whose bed is filled up with deposits down to a deph of 5 m.; several old river-gullies near Manggar, in which the lowermost deposits, containing the tin-ore, have been worked near mine No. 30, at a depth no less than 6 $^1/_2$ m. below the present sea-level.

In connection with the occurrence of these sunken and drowned stream-tinore deposits some remarks may be added about the influence of the surf on the unconsolidated freshwater-deposits during the rise of the sea-level, i.e. the submersion of the Sunda-peneplain. Although in that very shallow sea with hardly perceptible tides the action of the surf will not have been able to alter considerably the configuration of the sea-bottom, the incoherent bottom-deposits will no doubt have been modified more or less. As to the tin-islands, I believe that in the period of rise of the sea after the Pleistocene as well as during the periods of slight fluctuations of the sea-level in recent and subrecent times, both the stream-tinore deposits and the eluvial tin-deposits may have been modified more or less by the seawater, and especially as to the latter, may have been concentrated during this process. Instances of such modified deposits are, in my opinion, the tin-ore deposits which occur a little above the present sea-level in the island of Singkep along the beach to the west of the village of Dabo. They are, however, worked out now. (See fig. 2) [1]).

In the islands of Singkep, Billiton and Banca only comparatively small rivers rising on the hills of the ancient Sunda Land are concerned in the process just described. But we may reasonably expect as well that the courses of the larger streams draining the Sunda Land, which had cut their beds into the Sunda-peneplain, will not yet be entirely obliterated, although they were partly silted up when that plain was gradually submerged in consequence of the rise of the sea-level. If so, it must be possible to reconstruct their former courses from the isobathic lines in the present Sunda Sea.

However, the isobaths, as they are indicated on the charts, have been calculated from a limited number of soundings, at the very least rather more than a kilometer apart one from the other[2]). Moreover,

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[1]) A summary of discussions on the way in which tin-ore deposits originate and on the part played in this process by the seawater, may be found in an article which appeared when this paper was passing through the press, entitled: J. Rueb "Ontstaan der alluviale tinerts-afzettingen van Banka en Billiton". De Ingenieur 35e Jaarg. p. 21, 1920.

[2]) This holds good for these areas which have been fairly well explored bathymetrically, only few parts of the East Indian Archipelago being so well surveyed.

these soundings have been carried out on behalf of the navigation, consequently with the object to discover and to map the shallow parts rather than the deeper portions of the seas concerned.

Now when consulting the published charts [1]) and the original sheets one can, indeed, gather from them something (though not much) about the course of the larger rivers in the pleistocene Sunda-peneplain. First of all it appears that in this peneplain the chief watershed ran between the Bali Sea and the China Sea from Sumatra across the present islands of Banca, Billiton, through Karimata-strait, and further on across the Karimata-islands towards Borneo. It may be called the Karimata-divide. Again, from the trace of the isobath of 40 fathoms we conclude that from the China Sea a bay (see Fig. 1) cut deep into the land between the islands of Great-Natuna and Subi. At its entrance this bay is wide, but it narrows towards the south and passes into a large stream, which, coming from the south, empties itself into it. That main river flowed west of the Tambelan-islands and closely past the Badas-island and can be traced towards the south almost as far as Pedjantan-island.

This large river, which drained the whole Sunda-peneplain north of the Karimata-divide, presumably received on the right the Kapuwas and the Sambas as principal tributaries and on the left the Musi and the Djambi, which, however, may have united before they had reached the main stream. The submarine course of the Kapuwas is feebly indicated by a gully which is the direct prolongation of the Pungur-branch, while the ancient bed of the Musi is represented straight along the north-west coast of Banca by a gully with depths of 20—25 fathoms. On the existing charts the Kapuwas gully cannot be traced beyond Datu-island, the Musi-gully no farther than the meridian of the northern extremity of Banca, so the data, borrowed from the charts, render it just probable that the Kapuwas and the Musi did empty themselves into the main stream in the way indicated on map N°. 1. They do not afford conclusive evidence [2]).

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[1]) The charts which have been published, give only some of the soundings; their whole number is to be found on the original sheets which are kept in the department of hydrography of the Navy.

I take this opportunity of acknowledging my indebtedness to the Director of that Department, Captain PHAFF, for his kindness in granting me perusal of these original sheets.

[2]) After this paper has been read Mr. H. M. VAN WEEL, then commander of the surveying-vessel Brak, has been able to compile another chart with lines of equal depths from fresh data then available. From that map the powerful riversystem which

It has not been ascertained as yet in what direction the Indragiri and the Kampar reached the main stream; the only warrantable conclusion from what we know of the present submarine topography, is that from Singapore Strait a gully stretched eastward towards the Victory and Barren Islands, which thence may be traced to the main stream.

The water of the Siak-river and probably also part of the water of the Kampar-river discharged itself through Malacca Strait, where the isobath of 40 fathoms points to the presence of a deep bay from the northwest, into which the rivers of a part of Malacca and North-Sumatra at that time emptied themselves.

At the coast of the Bali Sea the Sunda Land was similarly indented to the north of the Kangean-islands by a deep bay. This bay received a large river, of which the isobaths of 40 fathoms and, more upstream those of 37 and 35 fathoms, enable us to trace more or less the course over a distance of about 350 km., from a point to the north of the Karimun djawa-islands in eastern direction along Bawean and then south-eastward to the East Bay mentioned before.

This large stream was formed by the confluence of the rivers of the portion of Sunda Land situated south of the Karimata-divide. It may be presumed that on the left it received the waters of the Kumai, the Sampit, the Katingan, the Kahajan, the Kapuwas Murung, and the Barito. A portion of the drowned Sampit-river, to a length of 65 km., is distinctly indicated by the isobath of 10 fathoms. It is likely that the Kahajan and the Kapuwas Murung united not far to the south of their present mouths and then discharged about 60 km. lower down into the Barito. The Barito very likely flowed in the Sunda peneplain in southern direction west of the Arends Islands and Great Salembouw, and then discharged into the great East Bay. Nothing more can be deduced from the existing charts about the course of these drowned rivers.

It may be surmised that at some distance from the north coast of the present island of Java also a large stream existed, which no doubt must have been fed by many affluents taking their rise on the mountainland of Java.

Finally the trace of a large river, which drained part of Sunda Land in he direction of Strait Sunda, may be seen in a narrow, deep trough, now from 30-40 fathoms below the sea-level, which is strikingly similar to the part of a drowned river broadening towards

drained the portion of the former Sunda Land north of the Karimata-divide, by the aid of the isobathic curves, can be reconstructed with a tolerable degree of accuracy.

the sea; it runs just to the south of the Hoorn-Islands and of Pajang-island, and may be traced thence over a distance of 70 km. in north-northeastern direction with an approximately uniform depth of 30 fathoms.

Data are wanting as yet to determine the further course of this stream and its branches.

e. Traces of revived erosion in pleistocene time.

Among the large rivers of Borneo there are some which possess terraces there where the low land passes into the upland. These rivers have cut themselves a bed into gravel formerly deposited by themselves. This must have taken place at a time when the erosive power of the rivers was stronger than at present, for now they have filled up their beds again, for the greater part, with finer deposits, sand and silt. These ancient gravel terraces have been observed by me at the Kapuwas near Sintang, a little above the confluence of this river with the Melawi and at the Katingan along its right bank, at and somewhat downstream from the place where it receives the Samba [1]). As late as the year 1894 gold was washed near Sintang from the gravel of these terraces. I feel inclined to think that the gravel of these terraces has been deposited in the late pliocene time and even in the beginning of the Pleistocene, when in Borneo denudation was not nearly so far advanced as it is at the present day. The origin of the terraces may readily be accounted for if we assume that during the glacial period the base-level of denudation was lowered about 75 m; this caused the fall of the rivers to become greater and the erosive power to be increased, and enabled the rivers to cut deep gullies into their own gravel deposits, which later on became broad valleys during the alternate periods of increased and decreased erosion corresponding to the successive glacial and interglacial periods.

At present the base-level of denudation is about as high as it was at the commencement of the Pleistocene just before the ice-age, but the island of Borneo having been meanwhile much denuded and eroded and thus having attained a stage of mature erosion, the rivers can only carry sand and silt at those places, where formerly gravel was deposited. The broad pleistocene valleys cut into the gravel terraces, consequently are now gradually filled up with sand and silt. Precisely such old gravel-terraces are found in the middle- and the upper-course of

[1]) G. A. F. Molengraaff. Geological explorations in Central Borneo p. 17—20 and p. 388, Leiden 1902. Geol. Verkenningstochten in Centraal Borneo p. 19—21 and p. 409—410, Leiden 1900.

several rivers in Sumatra; they are presumably also of pleistocene age and are due to the same causes as those of the rivers in Borneo, but, since the mountainland of Sumatra does not belong to the stable part of the Sunda Land, it may very well be that orogenetic movements have contributed to the origin of these terraces as well.

The distribution of Coral-reefs and their mode of development; the Great Sunda barrier-reef.

The distribution of coral-reefs in the Sunda Sea strikes us as being peculiar. First of all it is remarkable that in the Sunda Sea, which at the first glance appears to be situated very favourably for the development of corals, coral-reefs are poorly developed. Along the coasts of Borneo as well as along those of Sumatra and Java coral-reefs have developed so little that they are rarely marked on the hydrographic maps. Off the coasts it is just the same; there coral-reefs are equally rare. This is easy to understand if we consider that at its origin the Sunda Sea, as described above, must have expanded very rapidly, but that its depth, in the beginning, must have been very small; moreover, its salt-content was slight and its silt-content large, so that it cannot have afforded then favourable circumstances for the rapid spreading of reef-building corals.

An exception is formed only by the extreme marginal regions of the Sunda shelf-sea, where it borders on those seas, from where the water came that overflowed the former Sunda-peneplain. The marginal region I have in mind comprises first the archipelago to which the Natuna-islands belong, where well-developed fringing-reefs occur and also some detached coral-islands are found rising above the sea-level; secondly the archipelago of the "Duizend-eilanden" to the north-east of Strait Sunda, and lastly the Borneo Bank in the extreme east of the Sunda Sea. Apparently the Sunda Sea, which was originally very shallow and turbid, and rendered brackish by fresh water, was gradually stocked with corals from those three sides when it got deeper, clearer and salter; this process is perhaps still in progress.

Another question which claims our attention still more is the following: did reefs exist along the shores of the pleistocene Sunda Land, and if so, what became of them during the post-pleistocene submersion of the land? Have the fringing-reefs perhaps developed into reefs remote from the shore, into barrier-reefs, in the manner expounded for the first time by Darwin in his classical work on the origin of barrier-reefs and atolls? The shores here referred to,

are marked on the map (Fig. 1) by the 40-fathom line in the China Sea, in the Strait Sunda and towards the east between the coast of Borneo and the southern part of Strait Macassar.

From the deeper isobaths e.g. those of 100 and 200 m., it appears that from the coast of the former Sunda Land in pleistocene time a large shelf extended into the southern portion of the China Sea. On this shelf the depth of the sea increased very slowly and the sea-water was probably muddy, large rivers from the Sunda Land carrying their sediments into it, as may still be inferred from the character of the present bottom-deposits. The conditions for the development of shore-reefs, therefore, were unfavourable here. Hence one cannot be surprised to find now-a-days reefs rising from the ancient coast-line only here and there from a depth of 40 fathoms nearly up to the level of the sea. Nevertheless, it is a striking fact, that the only coral islands, now found in the South-China Sea, fairly follow the course of the 40-fathoms contour line drawn on our map, i.e. the probable coast-line of the submerged Sunda Land.

It is difficult to say whether or no along such a peculiar coast as the upper part of Sunda Bay must have been, the conditions for the forming of coral-reefs were favourable. As observed above, as early as in the pleistocene period the Sunda Bay cut deep into Sunda Land and was formed right to the south of the present Hoorn-islands and Pajung-island into a deep gully, which passed into a wide estuary of a stream coming from the north-east.

It is decidedly remarkable, though, that the area to the north-east of Sunda Strait, formerly the upper part of the Sunda Bay, contrary to all other parts of the Java Sea, abounds in true coral-reefs, which rise clear of the land from a depth of 20 fathoms or more, up to or near the level of the sea. Many of them, especially those rising up from a low depth, are most likely young and were generated by the union of small patches of corals, developed independently on loose rocks, as has been shown by SLUITER [1]). In shallow water, e.g. of a depth of 12 fathoms new coral islands even now continue to grow up from the bottom. However, with regard to those islands of the group of "Duizend-eilanden", which rise from a depth of 40 fathoms and more, as e.g. Pajung-island and others, I ascribe their origin to upward growth of reefs that had already been developed in the ancient Sunda Bay at the shore of the pleistocene Sunda Land before its submersion.

[1]) C. PH. SLUITER. Einiges über die Entstehung der Korallenriffe in der Javasee und Branntweinsbai, und über neue Korallenbildung bei Krakatau. Nat. Tijdschr. voor Ned. Indië XLIX p. 365 et seq. 1889.

At the former eastern coast of Sunda Land the relations are much clearer and less disputable. Here the stable Sunda Land borders on the unstable area of the sea of the Moluccas, more especially on the Strait of Macassar, one of the many deep-sea troughs that are still getting deeper and deeper, while other parts, the present islands, are still rising. In the pleistocene age this area between Borneo and Celebes was subsiding, and consequently the conditions for the development of a shelf on the east coast of Sunda Land at that time were unfavourable. The subsiding sea-floor brought the sediments, supplied by Sunda Land, down to such deep levels that shelf-formation was out of the question. The Sunda Land was thus bounded on the east by a deep sea, the present Macassar Strait, and its coast must have been steep on that side. There was no shelf. Thus ideal conditions for the growth of corals were realized: a deep sea, decidedly with clear and salt water, a strong surf, and a fairly steep, partly rocky shore. No wonder that along this coast a fringing-reef flourished well.

And what can be seen now?

On the most northern margin of the Sunda-shelf, the so-called Borneo Bank, stands a reef (Fig 3) rising as a narrow wall, interrupted in many places, from a depth of 70 to 90 m. to the surface of the sea, or nearly so. From this reef towards the land the depth of the sea decreases only very slowly from 70 m. downward; towards the sea, the Strait of Macassar, the depth increases very rapidly, in some places precipitously to 200 m. and more. A depth of about 1000 m. is found at a distance of some kilometers from this reef. This reef stands on the margin of the pleistocene Sunda Land; in pleistocene time, before the melting of the ice-caps in high latitudes, it was a fringing-reef attached to its shore and gradually as the Sunda-peneplain was being submerged by the sea, the corals were building the reef up. Nowadays it is a true barrier-reef, grown up round the disappearing Sunda Land in the manner as DARWIN supposes barrier-reefs to have developed generally.

Only this reef does not at first sight make the impression of a barrier-reef, because the land to which it belongs, has been flooded, in relation to the depth of the water, to such an exceptionally great distance. On close examination of the course of this reef, which may be termed the Great Sunda barrier-reef, it appears to begin at the Ambungi-reef, which belongs to the "Kleine Paternoster-eilanden". This small group of coral-islands, extending in east-westerly direction from Tandjong Aru to about 75 km. from the coast of Borneo, is perhaps to be considered as the most northern limit of the Sunda-

shelf on the east coast of Borneo. The coral-island of Ambungi lies about 120 km. to the south of the mouth of the Kutei-river. Our barrier-reef runs from the Ambungi coral-island in southeastern direction to a point opposite to and at the same latitude of Tandjong Ongkona on the coast of Celebes. There the reef is at a distance of 230 km. from the present coast of Borneo, but only 44 km. from that of Celebes. To the west of the reef, towards Borneo, the depth of the sea is very uniform, and nowhere exceeds 75 m.; on the east of the reef, towards Celebes, the depth of the sea increases abruptly to 200 m., from there rapidly to 1000 and somewhat further to 2385 metres. From this point the reef proceeds first towards the south-west, then towards the south-south-west to about 5°40′ southern latitude.

A well-nigh continuous portion of the reef, which at ebb-tide is laid bare in many places, lies between 4°′20 and 5°30′ southern latitude. It is known on the charts as the Laurel-reefs. The total length of the Sunda barrier-reef from Ambungi to 5°40′ southern latitude is about 500 km. The reef cannot be traced on the charts beyond 5°40′, but about 100 km. farther south it reappears again in the Kwong-Eng reef and may even be traced along a number of coral islands as far as the Kangeang islands, marking here again the extreme limit of the Sunda Shelf, i.e. of the submerged Sunda Land.

The gap of over 100 km. in the reef faces the entrance to a large inlet or bay, the East Bay, into which, in all likelihood, the large stream (or streams) discharged itself, which drained the Sunda Land in the pleistocene period in the direction of the most southern portion of Macassar Strait. This readily accounts for the absence of reefs there.

According to the sea-charts the Great barrier-reef [1]) is interrupted in many places and only occasionally reaches the surface of the sea; in most places it is found a little below the surface and only to the southwest of the Laurel-reefs its depth increases gradually. Probably on account of the insufficient salt-content of the water the conditions for the upgrowth of the former fringing-reefs were less favourable here than more towards the north in Strait Macassar.

[1]) NIERMEYER (l.c. p. 884 and Chart XIII No. 2) has already considered and described a portion of this great reef as a barrier-reef, but I think that he failed to see the relation between the genesis of the Borneo Bank and of this barrier-reef. Regarding the part of the reef that does not reach the surface of the sea between the Laurel reefs and the "Kleine Paternoster-eilanden", he puts the question: "Is a reef building itself up here from the seabottom?" My answer is obviously in the affirmative, but I conceive this building-up as having taken place not from a depth of 200 m., but from a depth of 75 to 90 m. simultaneously with the gradual rise of the sea-level after the glacial period. Let it also be stated here, that I do

The atolls and allied coral-islands, resting on truncated and submerged islands formerly belonging to the Sunda Land.

The southernmost, shallowest portion of Strait Macassar is separated on the north from the deeper part of that strait by two groups of coral-islands named the Kalu Kalakuang-islands and the Laars shoals and again on the south-east from the Flores Sea, by two other groups of coral-islands and atolls[1]), viz. the Paternoster- and the Postiljon-islands (Fig. 3). As to their structure they display a striking similarity.

1. *The group of the Kalu Kalukuang islands.* All of them are coral-islands. Most of them are rooted on the rim of a bank, which is rather flat, and lies on an average 20, nowhere more than 40 fathoms below the sea-level. Three soundings indicating depths of resp. 66, 90, and more than 100 fathoms, point to a division of the bank into two parts by a narrow deep strait.

All around the bank, which lies about 40 fathoms deep, the sea rapidly increases in depth from the edge of the bank. Upon this edge a coral-reef has grown up, which has been interrupted in many places. On the northern half of the bank this reef reaches the surface of the sea in many places; on the southern half this is not the case. Independent of the marginal reef, there arise here and there reef-structures from the upper surface of the bank as well, reaching the surface of the sea in some places. On the extreme northern part of the bank the reef-structures are arranged in the shape of a ring, thus forming a "faro" or atollon. The Kalu Kalukuang islands make up a composite atoll, the ring not being completely closed, but, especially in the southern parts, being broken over

not quite endorse the pronouncement made in the same paper on page 881: "no shelf, no barrier-reef." Even the reverse sometimes appears to be true, as no barrier-reef was formed along the Sunda Land in the South China Sea in spite of the presence of an extensive shelf, whereas in Strait Macassar, where a shelf was absent, a perfect barrier-reef has been developed. No more can I share the writer's opinion (p. 893) that the mode of development of barrier-reefs in the East-Indian Archipelago affords "fresh evidence to disprove DARWIN's theory according to which barrier-reefs have taken their origin from fringing reefs". In my opinion DARWIN's theory is supported by the mode of development of these reefs, which can only strengthen my conviction that "without subsidence of the land or rise of the sea level strengthen my conviction (which comes to the same) no true barrier-reefs and no atolls can originate".

[1]) Our knowledge of these coral-islands is still very insufficient. Renewed surveying may yield surprising results, as was the case with the latest survey of the islands of the Tukang besi group in the year 1916 and of the atoll of the Zandbuis-banks in the year 1910.

large distances. In structure the atoll bears a close resemblance to the composite atolls of the Maldive Archipelago, e.g. the Miladdummadula-atoll [1]), whose ring rising from the edge of the bank, which lies about 20—25 fathoms below the sealevel, is interrupted in very many places and also keeps below the sea-level over large distances. Only the shape of this Miladdummadula-atoll is drawn-out more in one direction than that of the Kalu Kalukuang atoll, the dimensions of the former being 146 × 31 km., those of the latter 98 × 58 km.

2. *The Postiljon- and the Paternoster-islands.* The description given of the Kalu Kalukuang-islands applies, in the main, also to these islands. They consist of three submarine banks with a depth varying from 17 to 40 fathoms. From the first bank, whose largest dimensions are, 140 × 50 km. two groups of reef-structures rise up to, or nearly up to the sea-level. They have chiefly grown up from the edge of the bank and are arranged in the shape of a ring and constitute the composite double-atoll of the Postiljon-islands. This double-atoll is made up of the southwestern Sarasa-atoll and the north-eastern Sabalana-atoll. Some of the reef-islands of the first atoll are again disposed into a ringlike arrangement, the Sapuka-faro. The north-eastern Sabalana-atoll is characterized, westward as well as eastward, by a remarkable projection or horn, towards the west the Bankawang-atollon, towards the east the Sabalana-atollon. The southwestern Sarasa-atoll might be looked upon as a very large faro or atollon, belonging to the entire Sabalana-atoll, in which case the term double-atoll could be relinquished.

The second bank, that of the Paternoster-islands, covering 115 × 26 km., of similar depth to the other, also bears, especially on its edge, which lies at a depth of about 40 fathoms, numerous coral-islands, arranged in the form of a wreath, and drawn out in one direction. Together they present a not typically developed atoll.

A little to the south of the Paternoster-islands lies a group of coral-islands whose beautiful atoll-shape became known by the hydrographical survey made by the surveying vessel Lombok in the year 1910. They form a nearly continuous ring consisting of three islets called the Zandbuis-Banks, Maria Reigersbergen and Huzaar. The lagoon is about 100 fathoms deep.

I presume that in the pleistocene age all these banks formed islands that belonged to Sunda Land, but had already been separated from it by subsidences in connection with the formation of the basins of the Bali Sea and Macassar Strait. The formation of these deep seas

[1]) A. Agassiz. The coral reefs of the Maldives. Mem. Mus. Comp. Zool. Harvard College XXIX p. 83 and Pl. 1—3, 1903.

was indicative of the orogenetic movements that are still in operation in the eastern part of the archipelago. It appears then, that already before the commencement of the Pleistocene the unstable East here encroached upon the stable West. Now, what is the history of these islands, the Kalukuang-, the Paternoster- and the Postiljon-islands? Initially they were raised at least 72 m. relatively to the sea-level, just as the entire Sunda Land. It is not known, but it is presumable that these islands, before the sea-level began to sink, were protected against the destructive effect of the surf, by fringing-reefs, and, accepting DALY's opinion expounded in his *glacial-control theory* [1]) we may conceive that in pleistocene time they were entirely abraded by the breakers and converted into banks of shallow depth. DALY believes that the abrasion and the truncation took place chiefly during the maxima of glaciation, i.e. the periods of lowest sea-level, through destruction by wave-action. It would appear to me that the abrasion and the truncation must have been especially strong and progressing during the periods of transition from glacial to interglacial, i.e. during periods of slow and prolonged rise of the sea-level. At the beginning of every interglacial period the abrasion and the truncation of the islands, which every time were peneplanized more intensely, was brought nearer to completion, so that at last, at the conclusion of the Pleistocene, the islands were completely truncated and were reduced to submarine banks, which consequent on the final rise of the sea-level after the close of the glacial period, were covered by the sea to a depth of more than 72 m. The coast-reefs, which happened still to exist at the close of the Pleistocene and the reef-structures which were generated here and there during the last submersion, grew up gradually with the rising of the water and were converted into atolls and atoll-like coral-islands, such as are found at the present day.

3. *The Spermonde Bank.*

Accepting the Kalukuang-, the Paternoster-, and the Postiljon-islands to have been portions of the Sunda Land, which have developed into coral-islands, one is easily led to suppose the large shelf on the west coast of South-Celebes, which bears the group of coral-islands known as the Spermonde Archipelago, to have been likewise closely related to the Sunda Land. The Borneo Bank and the Spermonde Bank have many things in common; both are on an average 50 and at

1) R. A. DALY. Pleistocene glaciation and the coral reef problem. Amer. Journal of Science XXX p. 297, 1910; Origin of the coral reefs. Science Conspectus I p. 120, 1911; The glacial-control theory of coral reefs. Proc. of the Amer. Acad. of Arts and Sciences LI p. 157, 1915.

most 75 m. below the sea-level; on the edge of the Spermonde Bank a barrier-reef has developed, which as to distinctness, is not inferior to the Great Sunda Barrier-reef, while the Spermonde Shelf, like the Borneo Bank is studded with a great number of reef-structures, which occasionally reach the surface of the sea. The Spermonde Shelf terminates abruptly at 4°16′ south latitude and the Spermonde Barrier-reef, which can be traced, although with interruptions, towards the north over a distance of 230 km., as a row of coral-islands, here gets attached to the coast-reefs; more to the north the coast of Celebes possesses only insignificant fringing-reefs.

It seems as if the history of the west-coast of South-Celebes in recent geological time has been similar to that of Sunda Land, contrary to the other parts of Celebes.

4. *The Laars Banks and the atoll Bril.*

The coral-islands, known as the Laars Banks and the atoll Bril, situated in the channel connecting the Strait of Macassar with the Flores Sea, warrant the assumption that this strait has become deeper in post-pleistocene time. The Laars Banks constitute together a composite atoll. The reef-structures form a ring with large gaps. They rest on a base which lies more than 100 fathoms deep, but is for the rest almost entirely unexplored. In the northern part the reefs have grouped themselves into a separate ring or "faro", which atollon is charted under the name of Laars-islands. The coral-islands of the Laars Banks have presumably originated in the same way as those of the Kalu Kalukuang Bank; it would seem then that formerly the Laars Bank was located at the same depth as the Kalu Kalukuang-, or the Paternoster-bank and like the latter belonged in the beginning of the Pleistocene as an island to Sunda Land. After the Pleistocene, however, the bank on which the Laars-atoll rested, subsided with the deepening of the water that unites Strait Macassar with the Flores Sea, and the coral-formations could only here and there, by upward growth maintain their position at or near the surface of the sea. The origin of the atoll Brill may be explained in the same way as that of the Laars-atoll. I am also inclined to believe that the Zandbuis-atoll and its lagoon with depths of more than 100 fathoms is founded on a bank which has subsided as late as the post-pleistocene time.

Oscillations of the sea-level in recent and subrecent time.

From the position of the terminal moraines and from other peculiarities of the territories that have been evacuated at the final

retreat of the pleistocene ice-caps, it has been possible to conclude that this retreat did not proceed continuously, but was interrupted by periods of stability and probably also of temporarily renewed growth of the ice. In historical times the same thing took place; the glaciers of the Alps were from the Roman era down to the last decades of the 16th century smaller than at this day, subsequently their area increased rapidly, and they generally remained more strongly developed than is the case now until about 1850; after this date they have almost continually decreased, but they are not by far so small now as, say, in the year 1570. These facts concerning the extension of the Alpine glaciers in historical times, points at least to one very marked oscillation, viz. slight extension between ± 50 A. D. and 1570; greater extension from 1570 to 1850 and once more less extension after 1850, which decrease is still continuing There is no reason for surmising that these fluctuations should not have manifested themselves in a similar way on all glaciated areas of the earth, and if this is the case they must have been reflected by corresponding slight oscillations of the sea-level. It may be accepted, therefore, that also at the coasts of the Sunda Sea something of such oscillations will be visible. Indeed, from some geologically well-known parts of the Sunda Sea phenomena have been observed which point to a slightly higher sea-level in recent geological time. VERBEEK records that at the coasts of Billiton [1]) and on the surrounding islands here and there elevated coralreefs are found, which, however, do not lie higher than 1 or 2 meters above high-tide level, and are often covered by coral-débris and sea-sand. According to VERBEEK the same occurs on the island of Banca [2]), while he adds also for this island that he knows of no places where coral-reefs are upheaved more than 1 or 2 meters above high-tide level. The position of these coral-reefs (the sea-sand proves nothing, as it may have been blown up by the wind there) proves that in comparatively recent time a slight oscillation of the sea-level has taken place, during which time the sea-level must have stood 2 meters, or somewhat more, higher than now. CORNETS DE GROOT [3]) believes that after the Tertiary the whole island of Billiton was uplifted some meters, because sea-shells have been found there of late-pleistocene

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[1]) R. D. M. VERBEEK. Geol. beschrijving van Bangka en Billiton. Jaarb van het Mijnwezen XXVI, 1897 pg. 81.

[2]) R. D. M. VERBEEK. l.c. pg. 62.

[3]) CORN. DE GROOT. Herinneringen aan Blitong. 's Gravenhage 1887, p. 200. 208 and especially p. 470–473.

(or recent) date[1]) in the stream-tin deposits in the mine Ditjang No. 8 in the district Tandjong Pandang, not far from the present beach. Still, from DE GROOT's description we are unable to infer whether or no this bed of stream-tin-ore (Kaksa) lies above the mean sea-level of this day, while VERBEEK reports that, most probably, it lies rather below the present sea-level. In 1911 I found a precisely similar deposit of recent shells in the Kaksa of the Merante-mine in the district of Linggang. This mine is not far from the coast and the bed of shells occurs about 8 meters below the surface. Though the exact height of the surface is not known, we may safely say that this bed, at any rate, does not lie above, but below mean sea-level. VERBEEK[2]) states the occurrence of just such shell-beds not only in the localities mentioned above, but also in mine No. 30 to the east of Manggar and in mine No. 1 in the district of Linggang, and adds that they are situated about at the present sea-level.

In connection with what has been said, I think that these occurrences of shells of very recent date, do not entitle us to draw conclusions about a possible slight uprise of the island with reference to the sea-level.

In the tectonically unstable portion of the Sunda Land, to which the greater part of Sumatra and Java belongs, various diastrophic movements are known to have occurred in pleistocene and post-pleistocene time. It is not my object to mention them or to discuss the way in which they originated.

The Sahul Bank.

The Sahul Bank is the submerged portion of a flat land, probably a peneplain that belonged to a large country of which in pleistocene time Australia, New-Guinea, the Aru-islands and some neighbouring islands formed a part. After the close of the pleistocene glacial period this low-lying land has been flooded consequent on the general rise of the sea-level. This flooded portion is the present Sahul Shelf (Fig. 1), which now lies on an average about 50 m. below the sea-level just about as deep as the Sunda Shelf.

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[1]) MARTIN has examinated these shells and comes to the conclusion "that the fauna in question belongs to a very recent past" and "that the fauna agrees with that of the sea surrounding the island of Blitong." See K. MARTIN. On a posttertiary fauna from the stream-tin-deposits of Blitong. Notes from the Leyden Museum Vol. III p. 17 and 19, 1881.

[2]) R. D. M. VERBEEK l.c. pg. 170.

I have not been able to collect sufficient data to unravel the geological history of this shelf. Suffice it to say that the rivers of Northwest Australia now emptying themselves into the Sahul Shelf-sea show the characteristics of drowned rivers. The fjordlike lower course of the Prince Regent River presents a typical example of a submerged or drowned valley.

Conclusions.

The conditions for shelf-building in pleistocene time were very favourable and reached an optimum in tropical regions at the close of the Pleistocene.

In tropical regions the sea-level stood in pleistocene time during the maxima of glaciation, at least 40 fathoms (72 m.) lower than at this day.

Malacca, Sumatra, Java, and Borneo were united into one continuous land, the Sunda Land.

In that Sunda Land the vast Sunda-peneplain has been developed into great perfection in the pleistocene age during the periods of low sea-level.

After the close of the pleistocene glacial period submersion of the Sunda-peneplain gave origin to the Sunda Sea and the Sunda Shelf, during optimal conditions for shelf-building.

The Great Sunda-barrier-reef originated by upward growth of the coast-reefs of the pleistocene Sunda Land during the period of general rise of the sea-level, which succeeded the ice-age.

The atolls and the atolliform coral-islands in the southernmost part of Strait Macassar have originated chiefly in the way which DALY in his *glacial control theory* puts forth as the typical mode of origin of coral-islands.

POSTSCRIPT.

After the above communication had been concluded an article by L. J. C. VAN ES [1]) reached me which treats of a subject, in many respects related to my own. I am not in a position to discuss here fully the conclusions arrived at by VAN Es, and to compare them with my own. I only wish to refer to some points treated in the summary of this article, which, for the rest, contains many interesting details. VAN Es imagines the island of Borneo to be united with Sumatra, and Sumatra also with Java and Malacca,

[1]) L. J. C. VAN ES. De voorhistorische verhoudingen van land en zee in den Oost-Indischen archipel en de invloed daarvan op de verspreiding der diersoorten. Jaarb. van het Mijnwezen XLV p. 255. 1918.

in late-pliocene time. The chart accompanying his paper gives his idea of the distribution of land and sea at that time. On that map also the courses of drowned rivers in that extensive late-pliocene and early-quaternary land are indicated, derived by the author from several of the isobaths in the present Java- and South-China Sea. He imagines in pleistocene time a subsidence of the land and a consequent transgression of the sea to have occurred beyond the present coastline. During that time barrier-reefs originated by upgrowth of the coast-reefs along the late-pliocene and early-quaternary coastline and also atolls arose, where small islands occurred. During the post-pleistocene time VAN ES assumes upheaval of the land and corresponding retreat of the sea. He conceives the upheaval, just as the preceding subsidence, to have been irregular, and most pronounced where previous earth-movements had been strongest.

The chief differences between his opinion and mine are:

1st. in pleistocene time VAN ES assumes subsidence of the land relatively to the sea-level, where I assume upheaval, whereas during the post-pleistocene time he admits upheaval where I assume subsidence of the land relatively to the sea-level.

2nd. VAN ES ascribes all shiftings of the coastline, the pre-pleistocene as well as the pleistocene and the post-pleistocene to orogenetic movements, whereas I claim the greater influence in pleistocene and in post-pleistocene time for oscillations of the sea-level in connection with the ice-age.

3rd. VAN ES does not distinguish between the stable and the unstable portions of the East-Indian Archipelago, i.e. between the two areas which, at any rate ever since the beginning of the Pleistocene, have been stable or unstable, whereas it is my opinion that only the great stability (which implies the total absence of earth-movements) of the greater part of the ancient Sunda Land can account for the remarkably uniform character of the present Sunda Sea and for the distribution and the mode of development of the coral-reefs in that part of the Archipelago.

II. BIOLOGICAL PART by MAX WEBER.

The theory of the subsidence of the Ocean-waters in the pleistocene ice-period and its geological and hydrographical consequences, so well expounded in the preceding pages by Professor MOLENGRAAFF, also concerns in many ways the biological sciences, first of all the faunistics and the zoo-geography of the Indo-Australian Archipelago, to what extent also the phyto-geography, I am not competent to judge.

It has long since been accepted by Zoo-geographers that in the latest Tertiary Sumatra, Java, Borneo and the intervening islands must have been interconnected by land, and must have been united with the peninsula of Malacca, consequently also with the Asiatic continent.

Only on the basis of this assumption could the faunistic uniformity of these islands be interpreted.

The faunistic differences, which also exist, are of two kinds. Some of them would have been brought about also if the vast land-complex that extended from the West-point of Sumatra to Macassar Strait — the Sunda Land of MOLENGRAAFF — had never been broken up into the present parts, simply on account of its vast extent and the difference in conditions of life as the immediate result. For others an explanation was found in the longer or shorter duration of the continuity of the now separated parts. It had been assumed, for instance, that Java first lost its connection with Borneo and Sumatra, while Sumatra remained longest united with the Asiatic continent.

The questions how this connection by land was brought about, and how it was broken up afterwards, led to various hypotheses, which were most often *ad hoc* and devised by zoologists and had no geological foundation. It is remarkable that we do not find among them what we will simply call CROLL and PENCK's theory, in which PENCK set forth the influence of the pleistocene ice-period on the ocean-level, in a comprehensive demonstration based on figures. Still, this theory would have afforded a sound interpretation of the recent changes of land and sea, required by Zoogeography for the facts observed. Nevertheless up to the present day it entirely escaped the notice of the Zoogeographers, who were engaged in the numerous problems regarding the Indo-Australian Archipelago.

This is all the more regrettable as, conversely, the zoogeography of the Archipelago could have yielded evidence to substantiate the validity of the CROLL-PENCK theory. In its turn it could then have shown again that it can afford data to prove geological hypotheses, and thus be subservient to the geologist, who is always occupied with problems bearing on the younger and the youngest history of our earth.

The fact that the CROLL-PENCK theory meets the requirements of zoogeography in a masterly way, speaks well for its validity.

But more cogent proofs of this validity might be given by zoogeography: one of them I will discuss here.

The supposed subsidence of the Java- and the South China-sea of 70 m. must also have affected the existing riversystems. That influence

was of no moment for the Westcoast of Sumatra and the South coast of Java. Here, as appears from the chart on page 411, the coast became only a few kilometers broader, the rivers lengthening in correspondence with it, which of course had no bearing on their fauna. On the other hand, that influence must have been very great elsewhere. A river discharging itself into the Java-, or the South China Sea, had to cut its way, when these seas were dried up, into the new land, in order to find a new outlet in the retiring sea; it had to receive newly formed affluents, which had to drain the newly shaped land. But, what is of still greater importance, is that two rivers, which are now separated, were mutually combined or formed part of a larger river-system.

Geology teaches us how the riversystem of Holland and Germany in the recent past differed from what they are now. How e.g. the Thames was a branch of the Rhine, how the Scheldt flowed in a different direction, how a large stream, which flowed through Germany from East to West, united the now separated Vistula, Elb and Weser.

In such a way the Mussi of East Sumatra may have been an affluent of a large river debouching into the China Sea, which also may have received the Kapuwas, discharging itself at the West coast of Borneo and presumably also continental Asiatic affluents. May be another river system emptied itself through Sunda Strait into the Indic, and transported besides the rainwater that fell on the land of the dry Java Sea, also the water of the rivers that in former times discharged themselves into it.

If there is a nucleus of truth in these speculations, we may suppose that some of it must be visible in the present-day fauna.

Let us suppose that the Kapuwas of West-Borneo formed, in the pleistocene, part of a riversystem, to which also belonged the Mussi of Sumatra. This would have occasioned an interchange of the fauna and mutual enrichment. But then this must be noticeable in a considerable faunistic similarity of these rivers that are now separated and have each an embouchure of their own.

The Mahakkam (Kutei) of the East coast of Borneo must behave quite differently.

This large stream, flowing into Macassar Strait was in no way affected by a decrease of 70 m. in the depth of this strait, whose depth amounts to some 1000 meters. It remained what it was, though its lower course was lengthened by several kilometers; no supply of water from other rivers, neither a change, nor an enrichment of its fauna could be expected.

The soundness of this reasoning, therefore, would be best testified

by a comparative investigation of the Kapuwas and the Mahakkam. Material for comparison could be procured by the fish-fauna, this being best known.

In selecting our fish-material we had to shift critically, and to make many restrictions. We had to exclude marine immigrants, indeed all so-called anadromous and catadromous fishes; secondly all fishes living in brackish water; only those species could be used for which seawater is an insurmountable barrier. For when at the close of the ice-period, which for the sake of convenience we will consider to have been a continuous period, the water resulting from the melting ice and snow gradually raised the level of the oceans, the seawater in the neighbourhood of the large river-mouths of Borneo and Sumatra will have been of a brackish nature prior to the present condition of the sea. At that time it was, then, possible for fish that could stand brackish water, to migrate from one river into another. That possibility disappeared only when the definitive salinity was established permanently.

After this shifting our working-material consisted only of two species of Notopterus, one Scleropages, 17 genera of Siluroids with 39 and 37 genera of Cyprinoids with 100 species, altogether 56 genera with 142 species.

The reliability of our results will increase with the extent of our material. We will, therefore, lay stress on the full significance of the number of 142 species. It appears from the fact that the number of true freshwater fishes, in the restriction given above, which excludes marine immigrants, amounts to only 60 species for the vast land-complex that comprises the Netherlands, Belgium, Germany and the Danubian countries as far as the Black Sea.

We have tabulated below our material taken from the Kapuwas and the Mahakkam, and have added those species that occur also in the rivers flowing into the Java Sea at the South Coast of Borneo. The table also contains those species that are found in East Sumatra, in Java and in rivers of the Asiatic continent (Malacca and Siam).

From this we see that of the 142 species only 52 are common to both rivers. Of the 90 remaining species 23 belong to the Mahakkam and 67 to the Kapuwas. Of the 67 species that do not occur in the Mahakkam 55 (82 %) are represented also in other rivers, viz. 75 % in the rivers of East-Sumatra. Only 12 species (1,8 %) are restricted to the Kapuwas, or are known from neighbouring rivers, also flowing into the South China Sea.

On the other hand the Mahakkam possesses 23 species which the Kapuwas lacks. But of these 23 species 17 (74 %) are indigenous

	Kapuwas.	Mahakkam.	South Borneo.	East Sumatra.	West Sumatra.	Java.	Continent. (M=Malacca; S=Siam)
Notopterus chitala (H.B.)	+	+	+	+	.	+	+
Notopterus borneensis Blkr.	+	.	+	+	.	.	.
Scleropages formosus (Müll. & Schl.)	+	+	+	+	.	.	.
Silurichthys phaiosoma (Blkr.)	+	.	+	+	.	.	M.
Wallago leerii Blkr.	+	.	+	+	.	.	.
Wallago miostoma Vaill.	+	+	.	+	.	.	.
Belodontichthys dinema (Blkr.)	+	.	+	+	.	.	M. S.
Silurodes hypophthalmus (Blkr.)	+	+	.	+	.	+	
Silurodes eugeneiatus (Vaill.)	+	.	.	+	.	.	.
Hemisilurus chaperi (Vaill.)	+	.	.	.	.	.	.
Hemisilurus heterorhynchus (Blkr.)	+	.	.	+	.	.	.
Hemisilurus scleronema Blkr.	+	.	.	+	.	+	.
Cryptopterus macrocephalus (Blkr.)	.	+	.	+	?	.	.
Cryptopterus bicirrhis (C.V.)	+	+	+	+	+	+	S.
Cryptopterus lais (Blkr.)	+	.	+	.	.	.	.
Cryptopterus cryptopterus (Blkr.)	+	.	+	+	.	.	M. S.
Cryptopterus limpok (Blkr.)	+	+	+	+	.	.	.
Cryptopterus apogon (Blkr.)	+	+	+	+	.	.	.
Cryptopterus micronema (Blkr.)	+	.	+	+	.	+	S.
Chaca chaca (Ham. Buch.)	+	.	+	+	.	.	+
Pseudeutropius brachypopterus (Blkr.)	+	.	.	+	.	.	.
Lais hexanema (Blkr.)	+	.	.	+	.	+	M.
Pangasius nasutus Blkr.	+	.	+	+	.	.	
Pangasius polyuranodon Blkr.	+	+	+	+	.	+	S.
Pangasius nieuwenhuisi (Popta)	.	+	.	.	.	.	.
Pangasius micronema Blkr.	+	+	+	+	.	+	.
Glyptosternum majus (Blgr.)	+	+	.	.	.	.	.
Bagarius bagarius (Ham. Buch.)	+	+	.	+	.	+	+

	Kapuwas.	Mahakkam.	South Borneo.	East Sumatra.	West Sumatra.	Java.	Continent.
Macrones nigriceps (C.V.)	+	+	+	+	+	+	M S.
Macrones micracanthus (Blkr.)	+	.	+	+	+	+	.
Macrones wolffi (Blkr.)	+	+	+	+	.	.	M. S.
Macrones nemurus (C.V.)	+	+	+	+	+	+	M. S.
Macrones planiceps (C.V.)	+	+	.	+	+	+	M.
Bagrichthys hypselopterus (Blkr.)	+	.	.	+	.	.	.
Bagroides melapterus Blkr.	+	.	+	+	.	.	S.
Leiocassis fuscus Popta	.	+	.	.	.	.	.
Leiocassis mahakamensis Vaill.	.	+	.	.	.	.	.
Leiocassis stenomus (C.V.)	+	+	.	+	.	+	.
Leiocassis poecilopterus (C.V.)	+	.	.	+	.	+	.
Leiocassis micropogon (Blkr.)	+	.	.	+	.	.	M.
Leiocassis vaillanti Reg.	+	.	.	.	.	.	.
Breitensteinia insignis Steind.	+	.	.	+	.	.	.
Gastromyzon borneensis Gthr.	+	+	.	.	.	.	.
Gastromyzon nieuwenhuisi (Popta)	.	+	.	.	.	.	.
Homaloptera wassinki Blkr.	+	+	.	+	.	+	.
Homaloptera ophiolepis Blkr.	.	+	.	+	.	+	.
Homaloptera orthogoniata Vaill.	+	+	.	.	.	.	.
Homaloptera tate regani Popta	.	+	.	.	.	.	.
Parhomaloptera microstoma (Blgr.)	.	+	.	.	.	.	.
Botia macracanthus (Blkr.)	+	+	+	+	+	.	.
Botia hymenophysa (Blkr.)	+	+	+	+	.	+	S. M.
Acanthopsis choirorhynchus (Blkr.)	+	+	+	+	.	+	+
Lepidocephalus pallens (Vaill.)	+	.	.	.	.	.	.
Acanthophthalmus lorentzi M. Web. & de Bfrt.	+	.	.	.	.	.	.
Acanthophthalmus kuhli (C.V.)	+	.	.	+	.	+	M.
Acanthophthalmus borneensis Blgr.	+	.	.	.	.	.	.

	Kapuwas.	Mahakkam.	South Borneo.	East Sumatra.	West Sumatra.	Java.	Continent.
Acanthophthalmus anguillaris Vaill.	+	.	.	.	.	.	.
Elxis obesus (Vaill.)	.	+	.	.	.	.	.
Vaillantella euepipterus (Vaill.)	+	.	.	.	.	.	.
Nemachilus longipectoralis Popta	.	+	.	+	.	.	.
Nemachilus fasciatus (C.V.)	+	.	.	+	+	+	.
Chela oxygastroides (Blkr.)	+	+	+	+	.	+	S.
Chela hypophthalmus Blkr.	+	.	.	+	.	.	.
Chela oxygaster (C.V.)	+	.	+	+	.	+	M.
Marcrochirichthys macrochirus (C.V.)	+	+	+	+	.	+	S.
Rasborichthys helfrichi (Blkr.)	+	.	+	+	.	.	.
Rasbora argyrotaenia (Blkr.)	+	+	+	+	+	+	.
Rasbora vaillanti Popta	.	+	.	.	.	.	.
Rasbora volzi Popta	+	+	.	.	.	.	.
Rasbora trilineata Steind.	+	.	.	+	.	.	.
Rasbora kalochroma (Blkr.)	+	.	+	+	.	.	M.
Rasbora einthoveni (Blkr.)	.	+	+	+	+	.	M. S.
Rasbora lateristriata var. sumatrana (Blkr.)	+	.	.	+	+	.	M.
Rasbora lateristriata var. elegans Volz.	+	+	.	+	.	.	M.
Rasbora lateristriata var. trifasciata Popta	.	+	.	.	.	.	.
Luciosoma trinema (Blkr.)	+	.	.	+	.	.	.
Luciosoma setigerum (C.V.)	+	.	.	+	.	+	M.
Luciosoma spilopleura Blkr.	+	+	.	+	.	.	S.
Leptobarbus hoevenii (Blkr.)	+	+	+	+	.	.	S.
Leptobarbus melanopterus M. Web. & de Bfrt.	+	.	.	.	.	.	.
Leptobarbus melanotaenia Blgr.	.	+	.	.	.	.	.
Rohteichthys microlepis (Blkr.)	+	.	+	+	.	.	.

CHART OF THE CORAL ISLANDS IN MACASSAR STRAIT

Fig. 3.

Scale: 1:2.000.000.

Solid line	Coast.
Dotted line	Isobathic curve of 40 fathoms or 72 meters.
Black	Coral-formations, projecting above the water or lying from 0 to 5 fathoms below sea-level.
Oblique stripes	Coral-formations, lying between 5 and 20 fathoms below sea-level.

	Kapuwas	Mahakkam.	South Borneo.	East Sumatra.	West Sumatra.	Java.	Continent.
Amblyrhynchichthys truncatus (Blkr.)	+	.	+	+	.	.	S.
Amblyrhynchichthys altus Vaill.	+	.	.	.	.	.	.
Albulichthys albuloides (Blkr.)	+	.	+	+	.	.	.
Dangila ocellata (Heck.)	+	+	+	+	.	.	.
Dangila fasciata Blkr.	+	.	.	+	.	.	.
Dangila cuvieri C.V.	+	+	.	+	.	+	M.
Dangila sumatrana Blkr.	.	+	.	+	.	.	.
Dangila festiva (Heck.)	+	.	+	.	.	.	.
Barynotus microlepis (Blkr.)	+	.	+	+	.	.	.
Thynnichthys vaillanti M. Web. & de Bfrt.	.	+	.	.	.	.	.
Thynnichthys polylepis Blkr.	+	.	.	+	.	.	.
Osteochilus borneensis (Blkr.)	+	.	.	+	.	.	S.
Osteochilus melanopleura (Blkr.)	+	.	+	+	.	.	S.
Osteochilus kelabau Popta	.	+	.	.	.	.	.
Osteochilus schlegeli (Blkr.)	+	.	+	+	+	.	S.
Osteochilus kahajanensis (Blkr.)	+	+	+	+	.	.	M.
Osteochilus repang Popta	.	+	.	.	.	.	.
Osteochilus vittatus (C.V.)	+	+	+	+	+	+	M.
Osteochilus hasselti (C.V.)	+	+	+	+	+	+	M. S.
Osteochilus kappeni (Blkr.)	+	.	.	+	.	.	.
Osteochilus brevicauda M. Web. & de Bfrt.	+	.	.	.	.	.	.
Hampala macrolepidota (C.V.)	+	+	+	+	+	+	+
Hampala ampalong (Blkr.)	+	.	.	+	.	.	.
Hampala bimaculata (Popta)	.	+	.	.	.	.	.
Labeobarbus tambroides Blkr.	+	+	.	+	+	+	.
Labeobarbus douronensis (C.V.)	+	+	.	+	+	+	.
Cyclocheilichthys heteronema (Blkr.)	+	.	.	.	.	.	M.

	Kapuwas.	Mahakkam.	South Borneo.	East Sumatra.	West Sumatra.	Java.	Continent.
Cyclocheilichthys janthochir (Blkr.)	+	.	.	.	.	.	.
Cyclocheilichthys apogon (C.V.)	+	.	+	+	.	+	+
Cyclocheilichthys repasson (Blkr.)	+	+	.	+	.	+	S.
Cyclocheilichthys lineatus (Popta)	.	+	.	.	.	.	.
Cyclocheilichthys armatus (C.V.)	+	+	.	+	.	+	S.
Cyclocheilichthys siaja Blkr.	+	.	.	+	+	.	M.
Puntius schwanefeldi (Blkr.)	+	+	.	+	+	.	M. S.
Puntius lateristriga C.V.	+	.	.	+	+	+	M.
Puntius tetrazona (Blkr.)	+	.	+	.	.	.	M.
Puntius fasciatus (Blkr.)	+	.	+	+	.	.	.
Puntius binotatus (C.V.)	+	+	+	+	+	+	M.
Puntius anchisporus (Vaill.)	+	+	.	.	.	.	.
Puntius sumatranus (Blkr.)	+	.	.	+	.	.	S.
Puntius bramoides (C.V.)	.	+	+	.	.	+	S.
Puntius collingwoodi (Gthr.)	+	+	.	.	.	.	.
Puntius bulu (Blkr.)	+	+	+	+	.	.	.
Puntius waandersi (Blkr.)	+	+	.	+	.	+	.
Puntius nini M. Web. & de Bfrt.	+	.	.	.	.	.	.
Balantiocheilus melanopterus (Blkr.)	+	+	+	+	.	.	S.
Barbichthys laevis C.V.	+	+	+	+	.	+	+
Labeo (Morulius) chrysophekadion (Blkr.)	+	.	.	+	.	+	S.
Labeo (Labeo) rohitoides (Blkr.)	+	.	.	+	.	+	.
Labeo (Labeo) pleurotaenia (Blkr.)	+	.	.	+	.	.	M.
Schismatorhynchus heterorhynchus (Blkr.)	+	.	.	+	.	.	.
Tylognathus hispidus (C.V.)	+	+	.	.	.	+	.
Tylognathus bo Popta	.	+	.	.	.	.	.
Tylognathus falcifer (C.V.)	+	.	.	.	+	+	.

	Kapuwas.	Mahakkam.	South Borneo.	East Sumatra.	West Sumatra.	Java.	Continent.
Gyrinocheilus pustulosus Vaill.	+	+	.	.	.	.	.
Paracrossochilus vittatus (Blgr.)	+	+	.	.	.	.	.
Discognathus borneensis Vaill.	.	+	.	.	.	.	.
Epalzeorhynchus kallopterus Blkr.	+	.	+	+	.	.	.
Crossochilus oblongus (C.V.)	+	+	.	+	+	+	M.
Crossochilus cobitis (Blkr.)	+	+	.	.	+	+	.

to the Mahakkam or other neighbouring rivers flowing into Macassar Strait. Of the 6 remaining species only 3 (13 %) occur also in East Sumatran rivers, while 3 other species are distributed over a wider range

When studying the well-defined genera it appears that of the 53 genera inhabiting the Kapuwas 20 (38 %) are lacking in the Mahakkam. It strikes us, however, that of these 20 genera as many as 18 are represented in the East Sumatran rivers. On the other hand, the Mahakkam possesses only 36 genera, 33 of which are also found in the Kapuwas, only 3 are wanting there, but they are not known to exist elsewhere, and are for the present to be considered as autochtonous.

We conclude, therefore, that the Kapuwas does not owe its far greater abundance of fish to autochtonous forms, but to such as occur also in East Sumatra. They point to a former connection with East Sumatran rivers, which, as alluded to above, finds an explanation in the CROLL-PENCK theory. This constitutes the great difference between the Kapuwas and the Mahakkam, though their sources are lying only at a few hours' distance from each other.

If my reasoning is correct, it must be so also for other groups of animals whose distribution underwent some change, anyhow in the pleistocene, not only for freshwater-, but also for land-animals. For the latter, the land of the Java- and the South China Sea, when laid bare, procured apparently the bridges required by zoogeography for emigration and immigration of animals.

Fundamentally this is quite correct; still even such evidence as

can be brought forward is not so cogent as in the case of the fish-fauna of the Kapuwas and the Mahakkam. When studying the problem, difficulties will crop up.

First of all the elements constituting a fauna are not of the same age. Older and younger strata occur with various possibilities of distribution.

Besides this historical factor, there are also various biological factors of different nature: Even though a species be induced to migrate to other quarters and may, by doing so, possibly enlarge its habitat, it can avail itself of this opportunity only when the conditions of life in the new abode meet the requirements of the species. — Furthermore, the question arises whether perhaps other influences in the ice-period affected the countries concerned or part of them. The fauna of Java e.g. has ever afforded special difficulties for the zoogeographers. It has already been alluded to in this paper that Java has long since been supposed to have behaved differently from Sumatra and Borneo, and consequently, also differs in its fauna. An attempt to account for this has been made by assuming that Java was the first of the islands to detach itself from the land-complex that united them. — But the faunistic peculiarities of Java may also have resulted from the occurrences consequent on the formation of the enormous range of volcanoes that runs through the island from West to East; the products of their eruptions (ashes, mudstreams, and the like) may also have influenced the fauna directly, or indirectly by modifying the climate (through intercepting the sunlight by the suspended dust of ashes scattered through the air, or by profuse rainfall).

Such questions will encumber the application of the CROLL-PENCK theory to the study of the distribution of animals in the Indo-Australian Archipelago, but a good many of these problems will admit of solution. For this theory offers a welcome basis for a number of hypotheses regarding former land-connections between the now separated islands, brought forward by zoogeographers to explain the facts observed. Moreover it clarifies our ideas with regard to the time at which the supposed land-connections originated.

The Great Sunda Islands have been discussed above.

But PENCK's theory also throws a new light upon the eastern half of the Archipelago. Here the distribution of animals led to the hypothesis that New-Guinea, together with the Aru Islands, Waigeu and the neighbouring smaller islands, formed one land-mass, that was connected with North Australia.

Those lands are now separated by shallow straits and a shallow

sea that covers the Sahul-bank. This bank is laid bare when the sealevel sinks ± 70 m.

In various writings I have tried to show that this condition was brought about in the pliocene and that the present status of land and water was developed in the pleistocene [1]).

Also P. and F. SARASIN assume, in their wellknown work on Celebes, a pliocene "Festlands-epoche" for the Archipelago, and R. D. M. VERBEEK wrote that at this day, and presumably ever since the Pliocene New-Guinea was separated from Australia by a shallow sea. Other writers (e.g. HEDLEY and MATTHEWS) seem to be satisfied in referring this occurrence to the "late Tertiary".

It was generally supposed that the process consisted in more or less local upheaval or subsidence of land or sea. Instead of these rather unfounded surmises, born of the wish to be able to dispose of land-connections, necessary for the zoogeographical theories, the CROLL-PENCK theory gives us a general view, yielding an actual basis. However, with this the supposed positive or negative subsidence is at the same time shifted from the Pliocene to the Pleistocene. This again lends support to our statement that the facts observed by Zoology speak for the validity of the CROLL-PENCK theory.

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[1]) A short survey of these speculations will soon be published in the Sitzungsberichte d. Heidelberger Akademie der Wissenschaften.

Geology. — "*On the Geological position of the Oil-fields of the Dutch East-Indies.*" By Prof. G. A. F. MOLENGRAAFF.

(Communicated at the meeting of June 26, 1920).

Experience has taught that the majority of the large oil-fields have originated in long enduring geosynclines, where these are marginal areas of sedimentation along the coasts of continents.[1]) In those geosynclinal belts, which are characterized by a long continued subsidence of the soil, the organic matter in the sediments, i.e. the remains of animal and vegetable organisms may, as the subsidence of the soil proceeds, successively be covered by layers of fine sediments. Thus, being shut off from water and air these organic remains may escape from destruction by oxydation. They may then be accumulated to a considerable thickness. As long as in such a geosynclinal coastal belt, subsidence prevails over sedimentation, the area remains covered by the sea; if, however, sedimentation gets the better of subsidence, the area may become land.

In the first case petroleum or allied hydrocarbons may be ultimately formed in the subsiding area; in the second case coal or allied substances may finally be found. A slow and gradual subsidence, the area meanwhile remaining all the time either low land or shallow sea, affords the most suitable conditions for the accumulation of such fossil fuels. Through the shifting of the equilibrium between the processes of subsidence of the soil and sedimentation, as well as through epirogenetic movements of land and sea relative to each other, every geosynclinal area may during its long life be land at one time and sea at another. Thus in the same geosyncline an accumulation of coal may take place at one time, and of petroleum at another; consequently in one and the same geosyncline coalbeds

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[1]) Among the recent publications bearing on this subject the following deserve special attention: M. R. DALY, Geosynclines and petroliferous deposits. Trans. Amer. Inst. of Min. Eng. LVII, p. 1054, 1918 and the discussion on it, ibid. p. 1065. W. F. JONES, The relation of oil-pools to ancient shorelines. Econ. Geol. XV, p. 81, 1920 and the discussion on it, ibid p. 350.

and oilbeds may [1]) occur alternately from the surface downward.

Broadly speaking the filling in such a geosyncline may be said to begin, as a rule, with the deposition of marine sediments with a monotonous microfauna, later and only when these sediments have attained a considerable thickness, they are overlaid by deposits of brackish-water, of fresh-water and perhaps by terrestrian deposits which will or will not alternate one with the other and possibly also with marine deposits.

Experience has also taught that in such marginal geosynclines during their long life folds may originate more or less parallel to the shore-line of the continent and at some distance from the shore. These folds may cause one or more rows of islands or a more or less continuous strip of land to emerge from the sea. Not seldom in such a case the folding process is attended with volcanic activity. The result may be that the portion of the geosyncline immediately bordering the continental shore, gets separated from the deeper ocean by a row of islands or a more continuous strip of land consisting of a system of one or more folded mountain-chains, which may even shut the inner portion of the geosyncline off completely, thus converting it perhaps into a freshwater lake for some time. It is evident that then the materials for sedimentation will be transported to the geosynclinal receptacle from two quarters, viz. from the continent and from the strip of land or mountain-range newly emerged from the sea, whereas prior to the folding the geosynclinal belt received its sediments from one side only, viz. from the pre-existing continent. In the case of violent volcanic action in the said strip of land, volcanic material will perhaps from that moment play a prominent part among the sediments which continue to accumulate in the geosyncline.

Finally experience has also taught that the geosyncline, which tends to get filled up completely, now that it has become narrower and receives sediments from two sides, mostly undergoes itself gentle folding. It is well known that this folding brings about a position of the strata, which is of prime importance for the working of oil-fields.

The outlines of the geological history of the largest and best known oil-fields of the world are similar to those described just now. Among the numerous instances only two, the oil-fields of Pennsyl-

[1]) Particular stress must be laid on the word "may", because it is possible that during the development of a geosyncline the conditions for the origin and accumulation of coal, of petroleum or of both are never quite fulfilled; in that case the geosyncline will remain sterile.

vania and those of Argentina, may be mentioned: in the Pennsylvanian geosyncline, which has originated as a belt marginal to the then North-American continent (the archaean Canadian shield built out southward), the sedimentation, as well as the folding of the Appalachians (Appellachia), which separated the inner portion of the geosyncline from the Ocean to the south-east, reached its maximum of intensity in Pennsylvanian time, and closed in Permian time; the oil-fields in the Andine portion of Argentina are marginal to the ancient South-American continent, which, in geological structure, exhibits striking similarity to South-Africa and the so-called Gondwana-land. The sedimentation in that geosyncline occurred in Jurassic and in Cretaceous time, while the folding which was attended by intense volcanic activity and gave rise to the Andes, terminated in Tertiary time. As a third instance the oil-fields of Venezuela may be quoted. As soon as one considers this mode of development of an oil-field to be the typical one, such a field must show the following features (see fig. 1):

1. a geosynclinal coastal belt G (fig. 1), being the depository of the sediments in which the hydrocarbons originate. The position of this belt will indicate in a rough way the original shore-line of

2. the continental area L, from which the terrigenous material is derived, which gradually has been accumulated in the marginal geosyncline. This area may also be called the ancient continental area or the primary area of denudation, because it existed already as a landmass before the geosyncline had originated.

3. the sea or ocean S, which, reckoning from the continent, lies on the other side of the geosyncline.

In the geosynclinal belt one can distinguish:

a. The portion near the land G_1 consisting of sediments deposited in a shallow sea or on a low land. These deposits consist preponderantly of terrigenous materials (limestones are rare) and contain coal-, or oil-beds or both. They are folded generally not very strongly during the last period of the orogenetic phase, which terminated a long era in the still longer life of the geosyncline.

b. The portion G_2 more remote from the land in which the sediments, for a great part marls and limestones, were deposited farther away from the shore of the continent than in the portion G_1. Generally this portion has been folded in a period of the orogenetic phase prior to the folding of the portion G_1. In that case the anticlinal parts of the folds had already emerged from the sea as rows of islands or more or less continuous strips of land or may be as lofty folded mountain-chains, whilst in G_1 the subsidence

of the soil and the sedimentation was still in progress. The belt G_2 generally has been upheaved, folded and compressed to a stronger degree than the belt G_1.

The folding of the belt G_2 is not seldom accompanied by volcanic activity causing the sediments in this area to be for the greater part composed of volcanic material. This area G_2 might, in contradistinction to L, also be called the secondary area of denudation.

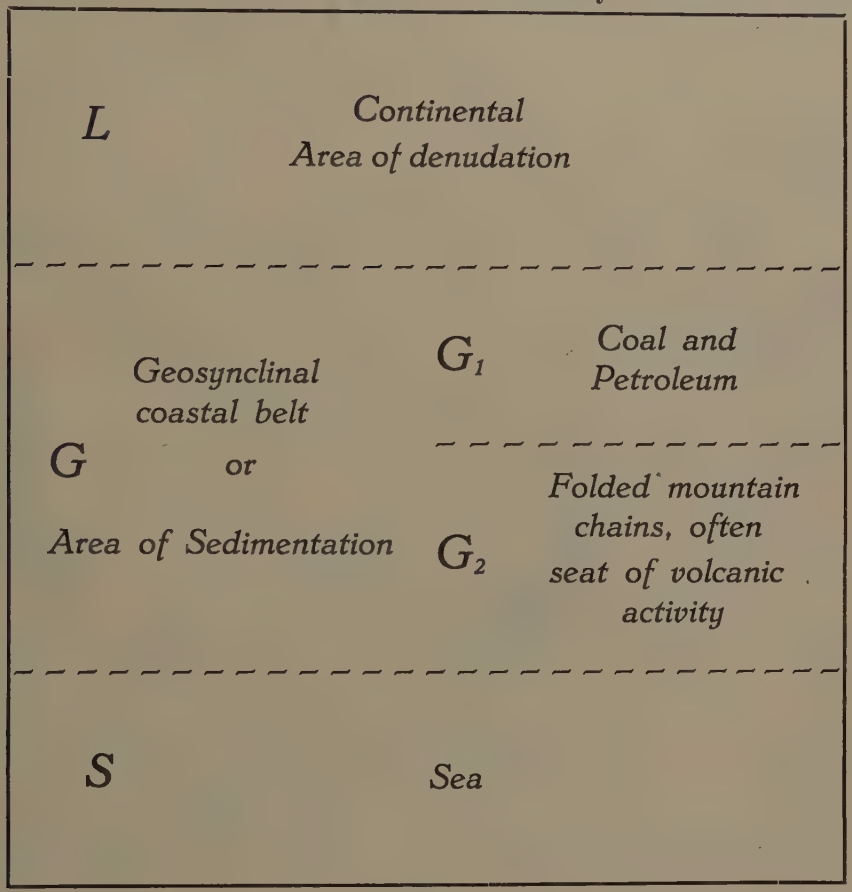

Fig. 1.

Our object in writing this paper is to discuss how far the position of the oil-fields of the Dutch East-Indies, fits in with the scheme sketched above.

The location of these oil-fields is marked on the accompanying sketchmap [1]) (Fig. 2). They are situated along the north-east coast of Sumatra, along the north coast of Java and along the east coast of Borneo. The sediments of which those oil-fields consist, have been deposited in the geosynclines in Tertiary, especially in Neogene time.

[1]) In compiling this sketchmap two authorities on the Australasian oil-fields KLEIN and RUTTEN kindly have procured me some valuable data.

There is in the Dutch East-Indies another oil-field of little importance in the island of Ceram, which probably dates from Mesozoic time. Its age, however, has not been quite proved. Another oil-field again, genetically closely connected with the Tertiary terranes mentioned above, is found in the East-Indian Archipelago outside of the Dutch possessions. It is the Tertiary oil-field situated in British North-Borneo and Serawak along the coast of the China Sea.

These latter territories will here be left out of consideration.

I. *East-Borneo.*

The geosynclinal belt *G* lies at the east coast of Borneo, along the strait of Macassar.

Fig. 2.

Black vertical lining: Neogene geosynclinal deposits, in which the occurrence of petroleum has not yet been established.

Solid black: Oilfields in Neogene geosynclinal deposits.

Dots: The dotted area represents the Sunda shelf; together with Malacca, Sumatra, Java and Borneo it indicates the largest extension of the Sunda Land in Pleistocene time.

The continental or primary area of denudation *L* is Borneo, the sea *S* is the Strait of Macassar, and between these two the Tertiary geo-

synclinal belt G is located, which has now been folded and converted into land for the greater part. The belts G_1 and G_2 gradually pass one into the other. The seaward strip G_2 is richer in limestones than G_1, which lies more landward, as has been shown by RUTTEN. In G_2 no volcanic action has taken place. According to RUTTEN the deposits in the Tertiary geosyncline of East-Borneo attain a thickness of about 5500 m. and comprise the entire Miocene, perhaps even a part of the Oligocene, and the Pliocene. Beds of lignite as well as beds of petroleum occur in this geosyncline. RUTTEN, from the differences in facies of the deposits, and before him VERBEEK concluded that the N.S.-shoreline of Kutei existed already in the Old-Miocene, and that at that time the Strait of Macassar had already been formed as a more or less deep trough. The oil-field of East-Borneo thus has been developed in a geosyncline, which lay between Borneo, a part of Sunda Land being the denudation-area from which it derived its sediments, and Macassar Strait being the adjoining oceanic area. This conception is accepted only provisionally, and some stress may be laid on the point that the geological position of Celebes relative to this geosyncline and to the Strait of Maccassar is not explained by it.

II. *Sumatra and Java.*

The geosynclinal belt G, to which the present oil-fields are confined (see map fig. 2) lies along the north-east and the eastcoast of Sumatra and the north coast of Java, bordering the Java Sea, the South China Sea and Malacca Strait. It is of Tertiary, Neogene age and the belt G_1, which contains petroleum and lignite in many places, is now slightly folded and the major portion has become land. Towards the ocean follows the adjoining belt G_2, which had already been folded and converted into a mountain-chain, whilst subsidence still continued in the portion G_1 of the geosyncline, and the process of sedimentation was still in progress there. The mountains of Sumatra, which I will designate here by the collective name of Barissan Mountains, represent one geanticline, and the row of the Mentawei-islands and others west of Sumatra represent another geanticline in these folded mountain-chains. More to the west follows the sea S, in this case the Indian Ocean. In the belt G_2 intense and prolonged volcanic activity has taken place in Sumatra as well as in Java; this activity commenced as early as the Old-Miocene. In the Miocene already volcanoes rose, presumably as a row of islands above the sea-level, for from that time andesitic material is found in the geosynclinal deposits of the belt G_1. But, where has one to look for the primary area of denudation L from which these geo-

synclinal troughs of Sumatra partly, and of Java entirely have derived the non-volcanic material now found deposited in them?

Where, in other words, is to be found the continental area *L*, to whose shores these geosynclines were marginal?

This continental area *L* lay to the north-eastward; it is the neogene Sunda Land, the greater part of which had been overflowed by the sea after the close of the ice-age. The part of Sunda Land which is now submerged is indicated by the dotted area in the sketch map Fig. 2, the contours of which have been derived from the present isobath of 40 fathoms. The dotted portion, however, does not represent its extent in Neogene time, but the largest extent which it reached only in Pleistocene time.

It appears, thus, that the geosynclines in which the three large oil-fields of the Dutch East-Indies, to wit those of Java, of Sumatra and of Borneo, have originated, during their development were marginal to one and the same continental area of denudation, the Sunda Land. This marginal position is now only noticeable in the Kutei-oilfield, of East-Borneo, because Borneo is the only portion of the former neogene Sunda-continent which still emerges from the sea as a small continental area. In order to understand the original relations between the area of denudation and its marginal geosynclinal belts, we must imagine the now overflowed portion of the neogene Sunda Land, viz. the Java Sea and the South China Sea, to be united again with Borneo, thus forming one continuous land. The assumption is admissible that originally the geosynclinal deposits constituted an entirely or almost entirely uninterrupted belt round the neogene Sunda Land. This is not the case now in the oil-fields hitherto known. The four oilbearing terranes, that of North-Sumatra, that of Djambi-Palembang, that of East-Java and that of East-Borneo are separated by large intervals. In Central-Sumatra, in the gap between the first-mentioned two territories, the geosynclinal deposits are present and petroleum may also occur in them, but, if so, presumably only at a great depth and overlaid by younger, posttertiary mostly volcanic deposits of considerable thickness. The same probability holds for the Lampong districts in the extreme south-east of Sumatra.

There is good reason to expect the occurrence of petroleum in deposits of the neogene geosyncline along the north coast of Java to the west of the peninsula of Japara, i.e. in the gap between the East-Sumatra- and the East-Java-oilfields. Here, however, the petroliferous strata will be overlaid, besides by more recent sediments of unknown thickness, also by the sea to a depth of 50 metres at the utmost.

The rapid improvements in the methods of boring will in the near future probably enable to prove conclusively which portions are still in existence of the deposits of petroleum and lignite which have originated in the far-extending geosynclinal trough marginal to the neogene Sunda-land.

CONCLUSIONS.

1. The three large petroleum-fields of Sumatra, Java and East-Borneo have originated in a similar way in neogene time in geosynclinal belts, marginal to the former Sunda Land, which after the close of the Pleistocene age for the greater part has been overflowed by the sea.

2. It may reasonably be accepted that, along the north-coast of West-Java, oilfields may occur below the surface of the sea overlaid by younger deposits down to a depth not established as yet. These oil-fields are closely connected to and fill the gap between those of East-Sumatra and East-Java.

3. It is improbable that in the eastern part of the East-Indian Archipelago [1]), more especially in the volcanic Lesser Sunda-islands, however much their geological structure may resemble that of Java, neogene lignite- or petroleum-deposits will be found, because one of the conditions for their genesis has not been fulfilled there, namely the presence of a geosynclinal belt of sedimentation, marginal to a continental area of denudation.

4. The opinion, enunciated by VERBEEK [2]) and RUTTEN [3]), that the Strait of Macassar had already been formed as a deep depression in Old-Miocene time, is supported by the way in which the oil-fields occur.

5. The fact that in Neogene time a continuous, or nearly continuous, geosynclinal area (which was folded afterwards) extended in a semicircle along the coast of the continental Sunda Land, makes it doubtful whether HAUG and P. SARASIN are right in considering the East-Indian Archipelago as the area where the Alpine and the circum-Pacific orogenetic systems meet or are interlaced.

This fact rather points to the conclusion, that it would be preferable to distinguish between a circum-Asiatic and an Australo-Pacific orogenetic system as those, which may be surmised to meet or to be interlaced in the East-Indian Archipelago.

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[1]) With the exception of New Guinea and the adjacent islands.

[2]) R. D. M. VERBEEK, Rapport sur les Moluques. Jaarboek van het Mijnwezen XXXVII, p. 823. Batavia 1908.

[3]) L. RUTTEN, Modifications of the facies of the Tertiary formations of East Kutei. These proceedings. Vol. XIX, p. 728, 1917.

Anatomy. — "*On a human ovary with a large number of abnormal follicles and the genetic significance of this deviation.*" By M. W. WOERDEMAN. (Communicated by Prof. J. BOEKE).

(Communicated at the meeting of June 26, 1920).

Last year, at the course of microscopic anatomy, sections of a human ovary, which had many peculiarities, were distributed among the students. I made a series of sections of 10 μ of that part of the ovary, that had not yet been cut into sections, in order to make an extensive study of the peculiarities found. After my examination of the preparations and the study of the very extensive literature, I think I am justified in adding another communication to that literature.

The origin of the preparation could not be traced. In the collection of materials of our laboratory it was only mentioned as "human ovary", without any further explanation. As it was not possible to make out, which of my predecessors had added the preparation to the collection, I am ignorant of the age of the individual, from which the organ was taken. It was fixed very well in formaline and was imbedded in paraffine. At a microscopic examination it was evident that there were a great many folliculi vesiculosi of DE GRAAF and a great many atretical follicles. At some places, I think I noticed some luteine cells. This is a sign that ovulation has taken place. Besides, the measurements of the organ in question and the comparison with ovaria of babies make it plausible that the ovary is from a mature individual. But this is only a hypothesis.

For in 1739 already, VALLISNERUS described the presence of ripe vesicles in a newly-born infant and according to E. RUNGE (1906) this phenomenon would appear regularly. The egg-cells would even be fit for fecundation and ovulation would take place. If this were true, the presence of large vesicles and ovulation phenomena would not prove that the individual was mature. But as KÄPPELLI and HEITZ examined more than 200 ovaria of newly-born animals, in which they found large vesicles, but never saw the slightest trace of ovulation, we should not accept without further evidence that ovulation takes place with babies. Whatever the case may be, it is very

probable that the individual, of which the ovary will be described here, is a mature woman. The preparation had several characteristics. First of all, it had a great number of ingrowths of the germinal epithelium, which covers the total organ as a single layer of cubic cells. These ingrowths are small tubes with a cylindrical round lumen, which is surrounded by a small number of bright, cubic cells.

The nuclei of the cells are lying almost in the centre of the cells. All the cells have about the same appearance. Most of the tubes are unbifurcated, only a few bifurcate. They generally do not proceed radially (towards the centre of the ovary), but very often they bend back under the germinal epithelium and proceed more or less parallel to the surface. Consequently one sees many rings of the epithelium under the germinal epithelium (transverse sections of tubes) in the sections. They are lying in the tunica albuginea and end, as far as I could see, blind. In the usual text-books of histology and microscopic anatomy these ingrowths of the germinal epithelium are not mentioned. But, in the text-books of veterinarian histology or those of embryology the occurrence of similar ingrowths in some animals and in human foetuses are mentioned. They are called "Keimschläuche" or "invaginations épithéliales". I will describe them here as "ingrowths of germinal epithelium", because a wrong idea of their genesis adheres to the name of "Keimschläuche".

In the second place the ovary showed a large number of cellular cords within the stroma. These cords are elongated and surrounded by a thin membrane of connective tissue and consist of very bright, regularly arranged, cylindrical cells (see fig. 1*a*). If they had a lumen, they would be exactly like glandular tubes. They have different names in the literature. The most usual one is "Markstränge" (cordons médullaires). Therefore, I will call them in future "medullar cords." The third and most obvious characteristic of the examined preparation is however the presence of a great number of abnormal eggfollicles. In many places, one sees the eggcells lying in groups and surrounded by a number of folliclecells, formed into, what is generally called "eggnests". Besides these eggnests [1]) in which I found as many as 9 eggcells, there were also vesicles (folliculi vesiculosi) with more than one eggcell. In those vesicles a large number of cumuli oophori, instead of a single one, occur (see fig. 1*c* and fig. 3). The greatest number I found was five. But beside the eggcells, which are lying in a real cumulus oophorus, one sometimes finds rudimentary eggcells in the vesicle.

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1) Eggball and eggnest may be used alternatively.

Fig. 1.

a. Medullar cord.
b. So-called eggball follicle.
c. So-called Schlauchfollicle.

Follicles with more than one eggcell are not unknown in man, however. The limit seems to be three. In some animals vesicles are found with numerous eggcells, this is even a normal phenomenon. The human ovary described here is already important owing to the rather large number of eggcells; it gains in importance on tracing the origin of the abnormal vesicles.

Fig. 2.
So-called Eggballfollicle.

The former conception of the genesis of the ovary was (briefly) the following:

From the germinal epithelium cellular cords penetrate into the ovary (occasionally they have rather the character of tubes or wedges). These so-called "Stränge" or "Schläuche" of VALENTIN PFLÜGER contain the primordial eggs and the future follicle cells. Gradually, connective tissue penetrates through these cords, destroys their connection with the germinal epithelium and divides them into cell-groups.

These cellgroups (Eggballs, WALDEYER) contain a number of eggcells and many follicle cells. Afterwards, every eggcell is surrounded by a single coat of folliclecells and the eggnests divide into a number

of eggcells, covered in this way (which are now called "primary follicles"). The ingrowths of the germinal epithelium are looked

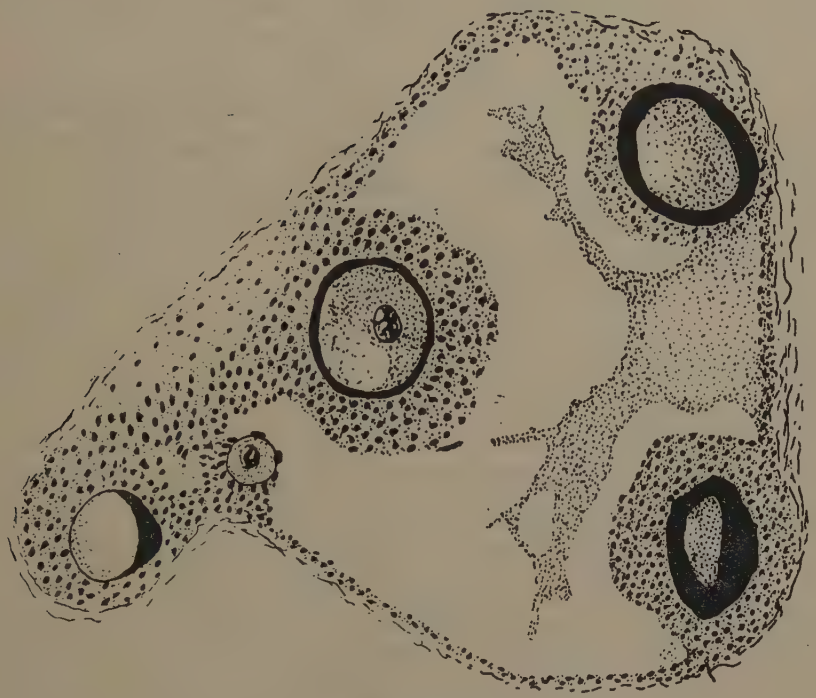

Fig. 3. Atypical follicle.

upon as the rests of tubes of Pflüger, originating from the germinal epithelium (Schmaltz in Ellenberger's Handbuch d. vergl. Mikrosk. Anat. der Haustiere, Bnd. 2, 1911). Consequently the name of "Keimschläuche" is given to those ingrowths. The medullary cords are also looked upon as rests of the proliferations of the germinal epithelium, viz. of the eggtubes of Pflüger. If the eggnests have been divided into primary follicles, vesicles, containing more than one eggcell would develop. According to Hellin (1895) there is a struggle between the connective tissue and the epithelium in the ovary, which generally ends in the victory of the connective tissue. If this is not the case, the division of eggnests into primary follicles, does not, or insufficiently, take place and afterwards a vesicle with more than one eggcell may originate. According to Schottlaender (1893) there is a regular relation between the growth of the connective tissue and the germinal epithelium. A disturbance in that regularity is the cause of the origin of the atypical vesicles. In later years, owing to a closer examination, a clearer insight was obtained

into the histiogenesis of the ovary. The excellent researches of COERT (Acad. Dissertation, Leiden 1898) and of VON WINIWARTER (Archives de Biologie, Tome XVII, 1900) may be mentioned here. As not all the embryological textbooks give the same representation of the development, I follow the report, which BÜHLER gives in HERTWIG's Handbuch (1906).

The ovary develops like the testis, from a special part of the posterior coelomic wall, in which the epithelium proliferates and forms a ridge (the so-called Genital-leiste or genital ridge). The line of demarcation between the epithelium of the ridge and the embryonic connective tissue is vague. The sexual cells become visible afterwards in the epithelium. Generally the line of demarcation between epithelium and mesenchyme becomes also clearer. It is irregular. The epithelium penetrates actually with fringe-like ingrowths into the mesenchyme. Those ingrowths are called "epithelial cords" (ALLEN calls them sex-cords). Sexual cells occur in these epithelial cords by the side of undifferentiated epithelium cells. An epithelial proliferation arises from the cranial part of the genital ridge, growing soon inwardly. COERT calls this mass the "reteblastem". When afterwards the genital ridge is tied off more and more, a small body, hanging on the posterior coelomic wall, originates (the undifferentiated sexual gland). There, where it is still connected with the backwall of the coelome, the "reteblastem" lies, from which a number of cords arise, which grow into the direction of the pronephros, as well as towards the centre of the sexual gland (rete cords). The sexual gland consists of a cortical layer, which is nothing but the epithelium of the genital ridge (Str. germinativum or epithelial layer) and an inner mesenchyme mass (Str. medullare). The germinal cords penetrate from the cortical layer into the Str. medullare. Sexual cells occur in the so-called rete-cords and especially in the germinal cords.

From this stage of development differentiation occurs between the development of the male and the female sexual gland.

The convoluted seminiferous tubules arise from the germinal cords, during the development of the testis, the tubules of the rete testis from the rete cords.

During the development of the ovary a thin layer of connective tissue (primary tunica albuginea) is formed between the cortical and the medullary layer. This tunica albuginea lets the epithelial cords pass at many places. A lumen is found, specially in the rete cords, less often in the germinal cords. The rete cords are also connected with the duct of the pronephros. Processes of development occur here, quite homologous to those, taking place in the testis. In the

primary albuginea, germinal cords and rete-blastem, we have to see the homologon of the testis anlage in man.

But in a female body, processes of development take place in the cortical layer besides. Proliferation of the epithelium has taken place here regularly, (in the mean time). The connective tissue of the primary albuginea penetrates into the cortical layer and the cortical epithelium penetrates in many places through the primary albuginea, so that the line of demarcation between cortical layer and medullary layer is again a very vague one. In consequence of the interweaving of the cortical layer and the connective tissue, epithelial cords and epithelial balls develop (not very distinct in man) from which finally the primary follicles arise by further proliferation of the connective tissue.

A complete epithelial layer remains finally at the surface of the ovary (germinal epithelium). The germinal epithelium still forms ingrowths, but they contain very seldom primordial eggs. In any case, they have nothing to do with the ovogenesis and with the eggtubes of Pflüger. The name of "Keimschläuche" is in my opinion less desirable. I should prefer the neutral name of "invaginations épithéliales" (von Winiwarter). They generally disappear later on. The germinal cords and the rete cords become rudimentary. The germinal cords grow into epithelial cords, lying in the medullary layer. Consequently they are generally called "medullary cords". A number of tubules are left from the rete cords. They are lined with cubical epithelium and lie in the hilus ovarii or even in the mesovarium. Some medullary cords are still connected with the rete. The rete itself may still be attached to the rests of the pronephros (epoophoron).

In the ovary described here (at least in the part I could examine) I did not find rests of the rete, but the ingrowths of the germinal epithelium and the medullary cords were present. With respect to the ingrowths of the germinal epithelium, the following may be said. They are probably a regular phenomenon in the ovaries of human foetuses. After birth they generally seem to disappear soon. A few communications on these ingrowths in infant ovaries are not very clear (cf. Schottlaender. Archiv für mikrosk. Anatomie. Bd. 41, 1893). They occur more frequently in young animals and they are even regularly found in adult dogs. (Schmaltz). From a figure in the book of Schmaltz we may conclude that they are considerably larger in the dog's than in the human ovary, I describe here.

There is a great deal of literature on the medullary cords, which von Winiwarter and Bühler cite principally. It is evident that they

are observed by many investigators in all kinds of animals during the development of the ovary. They generally break up into primary follicles before birth (Coert, von Winiwarter). Then the undifferentiated cells of the cords form the follicular epithelium for the eggcells in the cords. If the medullary cords do not break up into primary follicles before, they certainly do so shortly after birth. Bühler could not find them in the rabbit a few days after birth, though Coert and Winiwarter described them in the embryos of this animal. As von Winiwarter found them even 6 weeks after birth in the rabbit, it is evident, that we must take into consideration large individual differences. They seem to appear very regularly in the mature ovaries of carnivores and insectivores. Schmaltz mentions them as a regular phenomenon in the dog's ovary and less regular in the cat's.

Harz, Bühler, Paladino, van Winiwarter, Coert and Wichser found them in human embryos. Rielander (1904) found them in a girl of only a few weeks old. They consist of clear, protoplasmatic cells by a thin, structureless membrane. This agrees remarkably well with what I saw, but is different from what Schmaltz saw in the dog's ovary. The latter describes the cords as groups of granular cells with round nuclei, which sometimes surround a small lumen. In newly-born infants egg-cells occur besides (Bühler). Keibel and Mall (Handbuch der Entwickelungsgeschichte d. Menschen 1911) mention that the medullary cords are rather often found in the first years of life, but only seldom in the ovary of adult women. Bühler saw them in a girl of 2 years old, but not in older ovaries. The preparation described here is interesting, because it contains very clearly embryonic rests (ingrowths of germinal epithelium and medullary cords). The appearance of these rests is not so rare that it would justify this communication. I think, however, I can point out a connection between the presence of the medullary cords and the appearance of the numerous atypical vesicles.

While studying the sections of a medullary cord in the series (fig. 4) one perceives that egg-cells still occur in the medullary cords (cf. section 4 in fig. 4 and fig. 1*b*), but one can see at the same time that the medullary cord is able to swell at a certain spot and is transformed there into a vesicle, in which often more than one egg-cell occur.

It is obvious in the series that the medullary cord, after swelling and developing into a vesicle, afterwards regains its former appearance. This is an indication that the medullary cord of fig. 4 is not one that is accidentally connected with a vesicle, but that the

vesicle (Graafian follicle) is a modified part of the medullary cord. In fig. 1*c* we have a beautiful example of a vesicle, which is

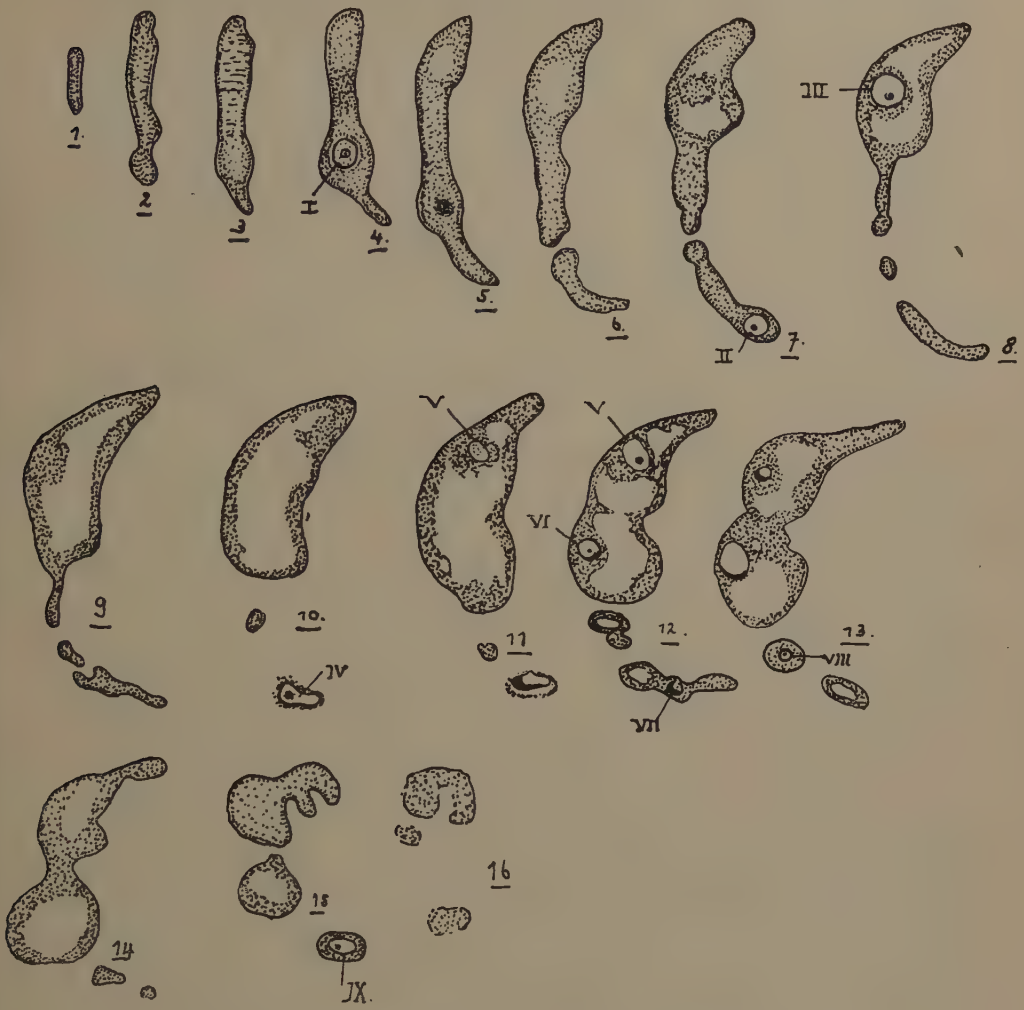

Fig. 4. 16 sections from a series of 80 (each of 10 μ).

merely a swollen part of a medullary cord. A rest of this cord is still seen attached to the vesicle. Though less clear the vesicle of fig. 3 shows such a rest. By these observations, I am convinced that a great number of atypical vesicles in the preparation, described here, originated owing to a proliferation of the epithelium in parts of the medullary cords. Afterwards those cells are vacuolised and a vesicle is formed. The remaining cells form a cumulus oophorus round the egg-cells, which originally occurred in the modified part of the medullary cord. As there are also groups of egg-cells, as reproduced in fig. 2, which must be looked upon as egg-balls, it is

not possible that all the atypical vesicles arise from the medullary cords but that also a great number originates in such egg-balls. I said already before that egg-cells are found in the medullary cords in embryos and also in newly-born infants. The fact that the medullary cords and the egg-nests originate from the same epithelium, explains this phenomenon sufficiently [1]). But all the investigators have found that those cords afterwards break up into primary follicles.

SCHMALTZ calls the eggcells, occurring in the medullary cords, strayed (verirrte) elements and supposes that they are reduced afterwards. In the case of dog, cat and other animals, in which the medullary cords remain, SCHMALTZ does not mention the occurrence of eggcells in those cords or their metamorphosis into vesicles.

The vesicle formation described before, I did not find mentioned anywhere, not even in the text-books of pathological anatomy.

Probably SCHOTTLAENDER (Archiv. f. mikrosk. Anatomie, 1893) found the same thing in man, as described before, but he explains them differently. There is only one text-book of histology (the antiquated book by BÖHM and DAVIDOFF) which, according to the representation of SCHOTTLAENDER, tells something more of the atypical vesicles than the other text-books I consulted.

SCHOTTLAENDER distinguishes "Eiballenfollikel" and "Schlauchfollikel". He calls the follicles, reproduced in fig. 2 and 3 eggballfollicles and those reproduced in fig. 1*c* and fig. 4 "Schlauchfollikel". According to him the origin of eggballfollicles is due to the fact that the eggballs are not broken up into primary follicles, owing to insufficient development of the connective tissue.

He thinks that the "Schlauchfollikel" develop from the tubes of PFLÜGER made free. (In his opinion the "Pflügersche Schläuche" are flattened and elongated eggballs). Undoubtedly SCHOTTLAENDER has seen in the human ovary vesicles, which were more or less modified cords and he described about the same phenomenon I saw. In the atypical follicles of fig. 4 and 1*c* however, I cannot see tubes of PFLÜGER, made free, partly because they do not occur in man according to BÜHLER, KEIBEL and MALL) and partly, because the investigation has taught us, that they are parts of epithelial strands, which undoubtedly must be looked upon as medullary cords.

Like SCHOTTLAENDER, I should prefer to distinguish two types of atypical vesicles: viz. "ballfollicles" and "cordfollicles". Probably, they both originate, owing to an insufficient anlage and develop-

[1]) It must not be left unmentioned that VAN DEN BROEK (1895) thinks there is a connection between the medullary cords and the mesonephros and GIANNELLI (1915) thinks they originate in the stroma ovarii.

ment of the ovarian connective tissue; the first because the normal rupture of eggnests into primary follicles failed to take place, and the last, because no primary follicles developed from the medullary cords. If this be true, the two kinds have also a different phylogenetic significance. The cord follicles arise from that part of the ovary which ought to be considered as the rudiments of the male part of the original hermaphroditic, sexual gland (Cf. KEIBEL and MALL, Handbuch d Entwicklungsgesch. d. Menschen, part I, fig. 8). The ball-follicles are developed from the female part. Though the sexual cells in the rudimentary male part (the medullary cords) undergo exactly the same changes as the eggcells and afterwards actually lie in the real "vesicles", it is yet possible that they are different from those developing in the female part of the sexual gland, (though this is of course not necessary).

One might imagine that they will never develop into eggcells, fit for fecundation, and that the vesicles, containing such cells, become atretical.

The follicles in the dog have generally more than one eggcell, but according to SCHMALTZ the larger vesicles contain as a rule only one eggcell, and consequently SCHMALTZ says the "mehreiigen Follikel" seem to disappear. According to BONNET (Lehrb. d. Entwicklungsgeschichte, 1918) in multiparous animals, two or more eggcells are discharged at the ovulation. BUMM (Grundrisz der Geburtshilfe, 12th Ed. p. 292), mentioning that STRASSMANN found in a human ovary two eggcells in nearly all the follicles, and even in the ovary of a woman, who died, while giving birth to twins, writes: "Da man bei Frauen, die nach Zwillingsgeburt starben oft nur *ein* corpus luteum nachweisen konnte, scheint die Entstehung der Zwillingsgravidität aus zwei Eiern *eines* Follikels nicht einmal ein besonders seltener Modus zu sein". Also, according to KEIBEL and MALL, vesicles with more than one eggcell may be the cause of twin gravidity. So it is very probable, that a number of follicles, with more than one eggcell, come to maturity and ovulation. But I wonder, are these not eggnest follicles?

The following consideration led me to this conclusion: In an ovary of an infant of 4 months old, of which I examined a series of sections, I found a great number of rather large folliculi vesiculosi and only some rests of medullary cords. Medullary cords are only seldom found in the calf (MAC LEOD), on the other hand HEITZ and KÄPPELLI found that shortly after birth, and even a short time before, a large number of well-developed Graafian follicles occur. This led me to the supposition whether these follicles, already

present at birth, could not have originated from the medullary cords. Afterwards it appeared that this idea was not a new one. SCHOTTLAENDER already is of the opinion, that most of the Graafian follicles of infants are eggnest- or Schlauch follicles, that is to say, follicles I described before as ball- and cordfollicles.

I recapitulate: BUNGE accepts that the Graafian follicles, present at birth in man, become mature and that ovulation takes place already in infants. On the other hand HEITZ and KÄPPELLI never saw any trace of ovulation in 200 ovaria of newly-born animals, in which they saw however many very large follicles [1]). I think the wisest is to accept (for the present) that the large Graafian follicles present at birth, do not develop, but are absorbed.

According to this idea, the follicles, with an abnormal number of eggcells, in adults, would not be cordfollicles, but ballfollicles. And these would be important for the origin of plurigravidity. We ought to point out besides that several authors talk of "Hauptei" and "Nebenei". That is to say that in a follicle with more than one eggcell one of them were to develop well and the others were to be reduced.

As rudimentary eggcells were often present in the atypical Graafian follicles observed by me, the possibility is not excluded that, owing to reduction of a number of eggcells from the atypical follicles, normal ones finally originate.

In a few words I will answer the interesting question whether a formation of new eggcells takes place in the medullary cords. I did not find anything that points to this fact. I can only say that I found in the ovary of a child of 4 months, which did not show any pathological deviation, primordial eggs in the germinal epithelium and also proliferations of this epithelium in which primordial eggs occur. This corroborates WALDEYER'S opinion and that of other investigators, that the formation of primary follicles still continues after birth, an opinion, which according to CUNNINGHAM and ROBINSON is based on observations in pathological cases.

SUMMARY.

1. In a probably adult human ovary were found: *a.* ingrowths of the germinal epithelium, which do not contain eggcells (the name

[1]) In a series of sections of the ovary of a young porpoise (Phocaena communis) I found only primary follicles. Clear medullary cords were absent, neither did I see secondary follicles. It is an open question whether 1. probably weakly developed medullary cords have been present, which do not give rise to vesicles, shortly before or after birth or 2 the follicles formed at birth, have all been reduced. I did not find traces of that reduction.

of Keimschläuche is less preferable) *b.* medullary cords which contain eggcells and at some places swell and develop into vesicles, *c.* a great number of follicles with more than one eggcell.

2. The atypical follicles are of twofold nature: there are ball- and cord follicles.

3. In the normal development of the ovary, owing to proliferation of the connective tissue, the eggballs and medullary cords divide into primary follicles, shortly before or soon after birth. In the preparation, described before, the development of the connective tissue was apparently insufficient.

4. It is possible that the large follicles occurring in old foetusus and in infants arise from the medullary cords. This is possible, because larger parts of the medullary cords develop into vesicles, but these may also originate from the primary follicles, which in normal circumstances originate from the medullary cords.

It is doubtful whether the opinion of RUNGE (that these vesicles contain eggcells fit for fecundation) is right, taking into consideration the genesis (medullary cord is homologous with the seminiferous tubules) and considering all we know on this subject in animals. The formation of vesicles from the medullary cords in the above-mentioned preparation, points to a disturbance in the development (a process, normally taking place at a very early age, found in an adult).

5. Normal vesicles may be developed from atypical ones by reduction of all the cells (Nebeneier) except one (Hauptei).

6. It is impossible to state whether the eggball or the cord follicle, or both can give rise to plurigravidity. In this case one ought to know whether the cord follicles are actually ripening to maturity.

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